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ENVIRONMENTAL MONITORING OF WATER SOURCES

LNEC final report of Marie Curie Transfer of Knowledge Action

Development of strategic academia-industry partnership in Romania for knowledge management in environmental friendly technologies "KnowEnTech"

PROJECT REFERENCE: MTKI – CT – 2005 – 029758

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Desenvolvimento de Parcerias Estratégicas entre a Universidade e Aa Industria na Roménia para a Gestão do Conhecimento em Tecnologias Amigas do Ambiente “KnowEnTech”

ENVIRONMENTAL MONITORING OF WATER SOURCES

LNEC Final Report of Marie Curie Transfer of Knowledge Action

Development of Strategic Academia-Industry Partnership in Romania for Knowledge Management in Environmental Friendly Technologies “KnowEnTech”

ABSTRACT

The present report contains a brief description of a two month stage in Bucharest, Romania, completed by the researcher Ana Patricia de Freitas Terceiro, from 4th of January until 28th of February 2009. The main activity developed during the stage consisted on writing the book entitled "Environmental monitoring of water sources" (authors: Patricia Terceiro, Rodica Ceclan, Ionel Popa, Virgil Racicovschi, Aurelia Meghea), also included in this report.

The stage was performed on the scope of a Marie Curie Action of Transfer of Knowledge entitled "Development of Strategic Academia-Industry Partnership in Romania for Knowledge Management in Environmental Friendly Technologies", aiming to support the development of long-lasting collaborations between industry and academia via the exchange of researchers.

The Transfer of Knowledge action is coordinated by the Universitatea Politehnica din Bucuresti and counts thirteen partners. LNEC (Laboratório Nacional de Engenharia Civil) is the host institution of the researcher, and the stage in Bucharest took place in both University Politehnica of Bucharest and ICPE (Research Institute for Electrical Engineering S.A.).

This report also contains a paper and a poster produced after the end of the stage in Bucharest, both presented at the 16th Romanian International Conference on Chemistry and Chemical Engineering, 9 – 12 September 2009, which took place at Sinaia – Romania.

RESUMO

O presente relatório contém uma breve descrição de um estágio de dois meses realizado em Bucareste, Roménia, efectuado pela Eng.ª Ana Patrícia de Freitas Terceiro, entre 4 de Janeiro e 28 de Fevereiro de 2009. A principal actividade desenvolvida durante o estágio consistiu na redacção de um livro intitulado “Environmental monitoring of water sources” (Autoria de: Patrícia Terceiro, Rodica Ceclan, Ionel Popa, Virgil Racicovschi, Aurelia Meghea), que é parte integrante deste relatório.

O estágio foi desenvolvido no âmbito do programa para Transferência de Conhecimentos (*Transfer of Knowledge*) da Acção Marie Curie intitulada “Development of Strategic Academia-Industry Partnership in Romania for Knowledge Management in Environmental Friendly Technologies”, cujo objectivo foi servir de base ao desenvolvimento de colaborações a longo prazo entre a indústria e a investigação, através do intercâmbio entre investigadores.

A Acção de Transferência de Conhecimentos é coordenada pela *Universitatea Politehnica din Bucuresti* e conta com 13 outros parceiros. O LNEC é a instituição acolhedora da Eng.ª Patrícia Terceiro e o estágio em Bucareste teve lugar na Universidade Politécnica de Bucareste e no ICPE (Research Institute for Electrical Engineering S.A.).

Este relatório contém também uma comunicação e um poster elaborados após o final do estágio em Bucareste, ambos apresentados ao “16th Romanian International Conference on Chemistry and Chemical Engineering”, que decorreu de 9 a 12 de Setembro de 2009, na Sinaia, Roménia.

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AKNOWLEDGEMENTS

Marie Curie Actions are intended to improve not only the number of European researchers but also their career prospective.

This stage is a part of the FP6 project Marie Curie ToK – IAP "Development of Strategic Academia – Industry Partnership in Romania for Knowledge Management in Environmental Friendly Technologies", contract MTKI – CT – 2005 - 029758, and I would like to thank the European Commission for the fellowship granted.

To Dr.-Ing. Habil. João Paulo Lobo Ferreira and Dra. Teresa Leitão, from LNEC's Groundwater Division, a special thanks for the opportunity for participating in this stage.

During my stay in Bucharest, I had the opportunity to work with Prof. Aurelia Meghea and Prof. Rodica Ceclan, and I would like to thank them for their help and support. And I can not forget to thank all my colleagues at the University, for the great working environment and for making me feel at home. I also dedicate my appreciation to Dr. Ionel Popa and Dr. Virgil Racicovschi, from ICPE, for their hospitality.

My stay in Romania would have not been the same if it wasn't for the great Portuguese community I met in Bucharest. To all of them a big thank you for all the great time we spent together.

MARIE CURIE TRANSFER OF KNOWLEDGE ACTION DEVELOPMENT OF STRATEGIC ACADEMIA-INDUSTRY PARTNERSHIP IN ROMANIA FOR KNOWLEDGE MANAGEMENT IN ENVIRONMENTAL FRIENDLY TECHNOLOGIES “KNOWENTECH”

STAGE REPORT

1 Introduction

The Sixth Framework Programme for Research and Technological Development (FP6) was launched by the Commission to help develop the European Research Area. This programme ran from 2002 to 2006 and it was a financial tool which the Commission used to put research policy into practice, and also providing the necessary financial support for scientific and technological development of projects.

Within FP6, the Human Resources and Mobility activity consists of a coherent set of actions, based on promoting the mobility of researchers. These were aimed at the development and transfer of research competencies, the consolidation and widening of researcher’s career prospects and the promotion of excellence in European research (European Commission, 2005).

The Transference of Knowledge fellowships can be implemented through two sub-schemes:

- Marie Curie Development Scheme (ToK – DEV) – aims to reinforce the research potential of host entities, with priority to entities situated in Less Favoured Regions of the Member States and in the Associated Candidate Countries;
- Marie Curie Industry – Academia Strategic Partnership Scheme (ToK – IAP) – aims to create and develop real strategic and durable partnerships between academic institutions and enterprises, in particular Small and Medium Enterprises (SME).

The present report refers to a Marie Curie Industry – Academia Strategic Partnership Scheme, which is bellow described, according to the Work Programme, section 2.3.1.3 (European Commission, 2005).

This scheme supports projects for the creation and development of strategic partnerships between the academic world and the world of enterprise, presented jointly by the participants, being on the one hand one or more universities/research Centers and on the other hand one or more companies, in particular SMEs. The different participants should be from at least two different Member or Associated States. These projects aim to allow the participants through the intersectorial exchange, in one or both directions, or experienced researchers to develop their knowledge by the integration of researchers in a different sectoral environment and to acquire and benefit from new knowledge when the researchers sent out return [to their organization of origin]. Such strategic research partnership projects can be coordinated either by an industrial or an academic partner.

Whilst respecting the normal rules for minimum participation of organizations for Member States and Associated States, intersectorial mobility is also allowed between two participants in the same Member State or Associated State, within the frame of the overall coherent transfer of knowledge plan for all the participants and up to a maximum of 30% of the researchers' months in the project.

Within this scheme, the industrial partners must be organizations operating on a commercial basis, i.e. companies gaining the majority of their revenue through competitive means with exposure to commercial markets, and will include incubators, start-ups and spin-offs, venture capital companies, etc. Preference will be given to projects that aim at fostering new, inter-sectorial, lasting research collaborations beyond the term of the contract, or at strengthening existing collaborations.

The minimum duration of a stage of the staff member is two months. If the coordinator is from industry, then there must be at least one participant from academia/public sector. On the other hand, if the coordinator of the project is an academic institution, then there must be at least one participant of industry, in addition to any other academic partners. The exchange should always be inter-sectorial, as it is not possible to have personnel mobility among participants from the same sector.

Short description of the project's objectives

The main goal of Marie Curie Action is to cover the most important needs of less favored regions and Candidate States, to determine a new economic step forward in order to ensure the local capabilities for participating in the EU efforts of social-economic growth.

The major objective of this project is to create and develop a real strategic and sustainable Academia – Industry partnership in Romania, in particular with SME's, based on an efficient knowledge/information and technology transfer activity through a new innovative structure under the form of a Science and Technology Park.

The main directions of the project are intended to raise awareness of the decision-makers towards the potential of knowledge for creation of welfare and, in the same time, to rise the self-confidence of the inventors and researchers that they are useful for the society. The project also aims to prepare skilled human resources able to co-operate with researchers and inventors, and the development of the capability of Romanian scientists, engineers and industrials to absorb the knowledge, information and environmental friendly technologies from the EU countries.

The specific objectives of the project are the following:

- Rising awareness on a competitive social-economical environment for SME’s;
- Promoting the best practices for breaking barriers in inter-sectorial communication;
- Creating the critical mass in technical and managerial resources and competencies to achieve a strategic Industry-Academia Partnership (IAP);
- Seeding knowledge in developing partnerships for technological transfer of the environmental friendly technologies.

These objectives should be achieved by mutual inter-sectorial exchange of specialists from Europe and Romanian host institutions, by means of ingoing phase, outgoing phase, while less than 30% of training activities should be exchanged by national specialists.

The project objectives are achieved by specific activities, split in 4 work packages, covering different topics:

- Policies for sustainable development of SMEs
- System of Knowledge Management in SMEs
- Managerial techniques for sustainable development of SMEs
- Sustainable development in friendly environment technologies
- Complementary skills development for SMEs in friendly environment technologies.

The topic 3.3.6 Environmental Monitoring of Outdoor Pollution Parameters, belonging to WP3, is the object of the research stage at Research Institute for Electrical Engineering S.A. – ICPE.

2 General Information

Researcher: Ana Patrícia Freitas Terceiro, Laboratório Nacional de Engenharia Civil, LNEC

Fellowship period: (Start Date – End Date): 04 / 01 / 2009 – 28 / 02 / 2009

Host Institution: Research Institute for Electrical Engineering, ICPE, SA

Host Institution Address: Splaiul Unirii 313, 030138, Bucharest, Romania

Daily Schedule: 9:00 - 17:00 (8 hours)

Scientist in charge: the general manager of the host institution, Dr. Dan Vergil Racicovschi, email: virgil@icpe.ro

3 Description of the Objectives/Activities of the Training Stage

The stage was meant to tackle the topic 3.3.6 of WP3, Environmental Monitoring of Outdoor Pollution Parameters.

According to project work plan, the subjects to be covered are:

- Courses to the staff;
- Sources of outdoor pollution;
- Assessment of outdoor pollution;
- Modeling of environmental dispersion of pollutants;
- Monitoring of air, water and soil pollution parameters;
- Contaminant remediation levels in water and soil;
- Source inventory and environmental quality standards;
- Occupational safety and health guidance;
- Trans-boundary outdoor pollution and inter-governmental regulatory policy;

- National and international requirements relating to environmental pollution.

The stage activities were conducted following the methodological approach of the project. Trials to acquire desired competencies by SMEs were done by meetings and two workshops organized by the host institution.

Thereby the stage contributed to the achievement of the general objectives of the project, developing an inter-sectorial transfer of knowledge from Academia to industrial sector, represented by SMEs, using best practices for removal of inter-sectorial communication barriers and concurring to the creation of the researchers critical mass needed to achieve an efficient Academia - Industry transfer of knowledge.

The topic itself contributes to the accomplishment of seeding in SMEs environmental monitoring, helping the small enterprises in raising their competitiveness.

The activities developed during the research stage consisted in:

- Daily activities at ICPE and University Politehnica of Bucharest;
- Bibliographic research (library and Internet) concerning the stage topics;
- Writing one book about the work package task;
- Workshops and meetings organized by the host institution.

The workshops, working groups and meetings with SMEs staff served as a Transfer of Knowledge modality and as a contact way between Industry and Academia partners which is useful in establishing future partnerships for new European projects development.

Annex 1 presents the preface and table of contents of the book written in the scope of the work package task, and the workshops’ programmes are presented on Annex 2 and Annex 3.

4 Further developments

Prior to the end of the stage, a paper and a poster were produced in order to be presented at the 16th Romanian International Conference on Chemistry and Chemical Engineering. The aim of the conference is to provide a forum for presentation and discussion on the main scientific achievements in chemistry and chemical engineering fields and to establish contacts between scientists and companies involved in research, development and production activities. The conference took place from 9th to 12th September 2009, at Sinaia, Romania. More information can be found at http://www.riccce16.upb.ro/.

The paper, entitled "Groundwater Monitoring", was written by Patrícia Terceiro, João Paulo Lobo Ferreira, Teresa Leitão, Aurelia Meghea, Rodica Ceclan and Mihail Ceclan and aims to disseminate the work developed during the joint Industry-Academia collaboration between Romania and Portugal. The Poster, by the same authors, briefly presents the more important issues focused in the paper. The paper is presented on Annex 4 and Annex 5 contains the Poster.

Lisbon, Laboratório Nacional de Engenharia Civil,

November 2009

VISAS

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REFERENCES

European Commission - Research Directorate General - Human Resources and Mobility (2005). Marie Curie Fellowships for Transfer of Knowledge (TOK). Handbook. Available in http://europa.eu.int/mariecurie-actions.

ANNEX 1 - Environmental Monitoring of Water Sources

Authors: Patrícia Terceiro, Rodica Ceclan, Ionel Popa, Virgil Racicovschi, Aurelia Meghea

Abstract

The present book was written during a two month stage in Bucharest, Romania, completed by the researcher Ana Patricia de Freitas Terceiro, from 4th of January until 28th of February 2009.

The stage was performed on the scope of a Marie Curie Action of Transfer of Knowledge entitled "Development of Strategic Academia-Industry Partnership in Romania for Knowledge Management in Environmental Friendly Technologies", aiming to support the development of long-lasting collaborations between industry and academia via the exchange of researchers.

The Transfer of Knowledge action is coordinated by the University Politehnica of Bucharest and counts thirteen partners. LNEC (Laboratório Nacional de Engenharia Civil) is the host institution of the researcher, and the stage in Bucharest took place in both University Politehnica of Bucharest and ICPE (Research Institute for Electrical Engineering S.A.).

Preface

In the last decades the knowledge in the groundwater field has been increasing, as aquifers are being more and more recognized as valuable and renewable natural resources. Groundwater extraction through wells and springs provide important water supplies for several regions in the world, not only for drinking water but also for agricultural and industrial uses. However, due to the pressure that human development put on soil and groundwater resources several aquifers are presenting contamination problems, which may cause the water to be unfitted for its uses.

At the European Union level, the need to protect groundwater in a concerted way has been highlighted with the publishing of important legislative instruments, like the Water Framework Directive (2000/60/EC) and, more recently, with a Daughter Directive: Directive 2006/118/EC on the protection of groundwater against pollution and deterioration. Both pieces of legislation refer the need to monitor groundwater systems, in order to better understand their state and to define protection measures to preserve the resources in a good state. Considering this, this book presents a general overview of groundwater monitoring procedures, a summary of approaches and techniques for sampling, analyzing, and evaluating the quality of groundwater.

Chapter 1 contains an introduction to water monitoring. Chapter 2 is focused on environmental pollution sources, in particular those that cause a risk to water bodies. Chapter 3 contains a brief description of different water bodies, also addressing water quality issues and main effects of pollution on groundwater. Chapter 4 refers to the current European legislation and the guidelines to plan a groundwater monitoring programme are described in Chapter 5. Chapter 6 addresses statistic in sampling and Chapter 7 is about monitoring the performance of analytical procedures. Chapter 8 approaches remediation of contaminated groundwater and, finally, Chapter 9 is about data presentation and analysis.

This book is the result of a joint collaboration between the National Laboratory for Civil Engineering – LNEC in Lisbon and Research Institute for Electrical Engineering – ICPE Bucharest, during the common activity developed within the frame of the European FP 6 project, Marie Curie ToK – IAP: "Development of Strategic Academia – Industry Partnership in Romania for Knowledge Management in Environmental Friendly Technologies" - contract MTKI-CT - 2005 - 029758 – coordinated by the University POLITEHNICA of Bucharest – project director Prof. Dr. Aurelia Meghea.

Authors

AKNOWLEDGEMENTS

The Authors would like to thank the European Commission for supporting them in writing this book, as a result of their research within the FP6 project Marie Curie ToK – IAP “Development of Strategic Academia – Industry Partnership in Romania for Knowledge Management in Environmental Friendly Technologies” - contract MTKI-CT -2005 -029758 – coordinator Prof. Dr. Aurelia Meghea.

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1 INTRODUCTION

The trend in analytical science is continuously moving towards instrumental methods of measurement. These determinations must be carried out in the framework of a detailed understanding of both physics and chemistry of the systems being analyzed, and the measurement carried out with the closest regard for the integrity of the transmission process.

The necessary tetrahedron of researchers, investors, equipment suppliers, and users should particularly watch for analytical instrumentation openings in the growth of microelectronics, biotechnology, and the requirements for environmental conservation.

There is a considerable need to monitor the quality of waters and effluents to protect the environment and provide drinking water.

Neither monitoring by on-site monitors, nor laboratory analysis offer comprehensive performance.

The options available for water quality monitoring are discussed with a view to indicate the practical problems that arise in monitoring, together with some solutions that have been found to be effective.

Monitoring of water bodies is required to meet various needs:

- To ensure that statutory quality standards are met. These include local, state and European Community requirements.
- To ensure that the water resources quality used for drinking water supply is adequate.
- To detect and identify pollution.
- To check plant performance and signal potential pollution.
- To provide quality data over a period for trend prediction, planning and design.

Regarding groundwater in particularly, the typical research projects aim at:

- Characterizing natural or reference conditions.
- Characterizing possible pollution effects, their degree, and spatial extension.
- Monitoring water conductivity on coastal aquifers, as seawater intrusion may result on water quality problems.
- Measuring depth to water table and identifying trends along time.
- Protecting and managing the groundwater resource, ensuring that it remains suitable for domestic, industrial, agricultural, and environmental uses.
- Monitoring the effectiveness of management options.
- Preventing land subsidence that occurs when large amounts of groundwater have been withdrawn from certain types of rocks. The rock compacts because the water is partly responsible for holding the ground up. When the water is withdrawn, the rocks fall in on themselves.

The responsibility of the Water Authorities should encompass maintaining the quality of the entire water cycle. Thus, attention must also be given to protection of underground aquifers, surface waters used for purposes other than drinking water supply, such as leisure activities, and to actions which may subsequently affect water quality, for example effluent discharges from industry and sewage works

The quality of effluents and waters discharged to the marine environment is another area where monitoring of pollution is important and is becoming an area of major public concern.

Various industrial plants may require effluent monitoring within their own boundaries to avoid pollution and to ensure efficient plant operation.

1.1 The need for monitoring

Checking the water quality can either be carried out by taking individual (“grab”) samples and returning these to a laboratory for analysis (some local restricted analysis could be possible), or by attempting to monitor the water quality by using on-site equipment. Both approaches are commonly used but neither is perfect, and the simultaneous and careful use of the two methods will offer the best detection of pollution.

At first sight, on-site monitoring would appear to offer every advantage of laboratory analysis and have the principal overriding advantage of being constantly vigilant. In reality, on-site monitoring has limitations that must be taken into account before installing such systems.

1.2 On-site automatic monitoring

The advantages of on-site automatic monitoring are:

- Analysis is carried out at the sample source with minimal time delay;
- Continuous or continual monitoring of sampled source giving data around the clock;
- Reproducible sampling and analysis enabling archive data to be gathered;
- Sample is immediately analyzed so that changes in composition cannot occur;
- Telemetered alarms or automatic controls are possible based on the analytical data;
- Large sample volumes are possible;
- Current status can be interrogated;
- Work force requirements are low;
- Analytical cost once the system has been installed is low.

The disadvantages of on-site automatic monitoring are:

- Difficulties in providing all the necessary tests;
- High initial capital costs, duplication of instruments;
- Difficulties in relocating automatic monitors;
- Regular maintenance and standardization procedures are required;

- Highly skilled personnel needed for ensuring instrument performance;
- Problems with vandalism on sites where the public may have access (with or without authority);
- Large number of results require automatic data processing;
- Establishing confidence in alarms and eliminating false alarms.

1.3 Grab sampling and subsequent laboratory analysis to complement on-site monitor analysis

The advantages of grab sampling and subsequent laboratory analysis to complement the on-site monitor analysis are:

- Virtually no limit to the number and nature of the species that can be analyzed;
- Very sophisticated analytical equipment and techniques can be used;
- Flexible approach to the analysis which can be performed;
- Samples can be taken from any location.

The disadvantages of laboratory analysis are:

- Analysis occurs some time after sampling making rapid decision difficult;
- Some determinants may alter with time (such as pH);
- In real time only a few samples are taken which may give “snapshot” results which are not typical (e.g. water bodies would not be routinely sampled at night);
- Manpower requirement for sampling, transportation and analysis is high;
- Possibility of contamination of sample during transport to laboratory.

2 ENVIRONMENTAL POLLUTION SOURCES

2.1 Water Pollution

Even though pollution had been known to exist for a very long time (at least since people started using fire thousands of years ago), it has seen the growth of truly global proportions only since the onset of the industrial revolution during the 19th century. The industrial revolution brought with it technological progress, such as discovery of oil and its virtually universal use. In parallel, the scientific development led to a better understanding of pollution problems and to the study of mitigation actions and measures directed to the environmental protection.

Environmental pollution can be defined as the contamination of the physical and biological components of the earth/atmosphere system to such an extent that normal environmental processes are adversely affected. There are three main types of environmental pollution: air, water, and soil. This chapter is focused on water pollution.

Until recently, water pollution was viewed primarily as a threat to human health because of the transmission of bacterial and viral waterborne diseases. In less developed countries, diseases transmitted through water remain a major public threat. On the other hand, in developed countries, due to water treatment technologies, microbial contamination in water is almost eradicated

Water pollution results on the loss of any of the actual or potential beneficial uses of water caused by any change in its composition due to human activity. There are many specific causes of water pollution, which fit on one of these two broad categories: Point Pollution or Non Point Pollution.

Figure 1 – Example of environmental pollution sources

2.2 Point Pollution

Point source pollutants in surface water and groundwater are usually found in a plume that has the highest concentration of the pollutant near the source (such as the end of a pipe) and diminish further away from the source. In this case, harmful substances are emitted directly into a body of water.

Point source pollution generally comes from the volume of wastewater discharged from the pipes of industrial facilities and municipal sewage treatment plants into rivers, streams, lakes, and the ocean. Sources of wastewater may include domestic wastewater inflow, commercial operations such as restaurants, food processing facilities, and industrial facilities.

Wastewater is considered a potential source of pollution because it may contain organic and inorganic materials that can be hazardous to both humans and other life forms, especially if untreated or only partially treated. In many streams, treated wastewater may actually be cleaner than what is already contained in the stream; however, treated, untreated, or partially treated wastewater may also contain small amounts of radiation or toxics that increase the temperature of waters, affecting aquatic wildlife and habitat. Finally, discharged wastewater may also lower the amount of dissolved oxygen in the receiving stream (oxygen is required by microorganisms that consume the organic material).

Wastewater from manufacturing or chemical processes in industries also contributes to water pollution. Industrial growth, however essential, pollutes and virtually poisons water bodies, either directly or indirectly. While some industries release their effluents into rainwater drains that ultimately end up in a river itself, others dump their solid wastes such as slag over vast areas surrounding their sites. In some cases, industries discharge their effluents into the municipal sewage network, which might cause damage to the system, to the flow of sewage or to the treatment process.

Even though industrial effluent characteristics depend of the industry type and technology used by the facility, industrial wastewater usually contains specific and readily identifiable compounds (e.g.: organic loads, heavy metals, chemical and toxic substances).

One of the most important types of pollutants are oxygen demanding substances, because these materials decompose in the water course and can deplete the water’s oxygen and create anaerobic conditions. These substances might be discharged from milk processing plants, breweries or paper mills, as well as municipal wastewater treatment plants. Suspended solids also contribute to oxygen depletion, besides creating unsightly conditions and causing unpleasant odors.

Nutrients, mainly nitrogen and phosphorus can promote accelerated eutrophication (see Chapter 3.1.2 for more details), and some bioconcentrated metals can adversely affect aquatic ecosystems, as well as make the water unsuitable for human contact or consumption (Peirce *et al.*, 1997).

Another industrial waste discharge into water is heat. Heated discharges may drastically alter the ecology of a stream or lake, as it lowers the solubility of oxygen in the water, once gas solubility in water is inversely proportional to temperature. As a result, the amount of dissolved oxygen available to breathing species decreases. As the level of dissolved oxygen lowers, metabolic activity of aerobic aquatic species increases, thus increasing oxygen demand (Peirce *et al.*, 1997).

2.3 Non Point Pollution

As rain falls and strikes the ground a complex runoff process begins, carrying with it dissolved and suspended material from the watershed into adjacent streams, lakes, and estuaries. Human activities, like farming, harvesting trees, or constructing cities led to disruptions in vegetation and soils, increases in impermeable surfaces, introduction of agricultural chemicals, fertilizers, and animal wastes into the watershed, together with the disposal of several types of atmospheric pollutants. The combination of these types of pollution from diffuse, widespread sources is called non point pollution.

Non point pollution is characterized by a difficulty in finding specific discharge areas and for having a large number of polluting points. This type of pollution is usually found spread throughout a large area. Some examples of non-point pollution sources include runoff from agricultural and forestry land, storm water runoff from urban areas and discharges from on-site sewage disposal systems.

Runoff from agricultural land typically contains high concentrations of suspended soils, dissolved salts, nutrients from fertilizers, biodegradable organic matter, pesticides, and pathogens from animal wastes. Activities like construction and silviculture, which disrupt the vegetation cover or soil surface, will contribute with sediments and nutrients as phosphorus to surface runoff. Runoff from silviculture sites may also contain herbicides, applied to control the growth of undesirable plants. Urban runoff often contains high concentrations of suspended and dissolved soils, nutrients, and pesticides from landscaped areas, toxic materials, oil, and grease and hydrocarbons from roads. It also may contain pathogens from pet wastes and leaking septic tanks, synthetic organics such as detergents or chemical solvents and other compounds that accumulate on impermeable surfaces, or are carelessly poured down storm drains (Peirce *et al.*, 1997).

Focusing on agricultural areas, the primary pollutants are nutrients (particularly nitrogen and phosphorus), sediment, animal wastes, pesticides, and salts. The processes by which these compounds affect both surface water and groundwater were already referred above, together with irrigation practices when they are not efficient. Regarding soil, various farming activities result in the erosion of soil particles. Salt accumulation on irrigated soils causes the most damage and loss in their category.

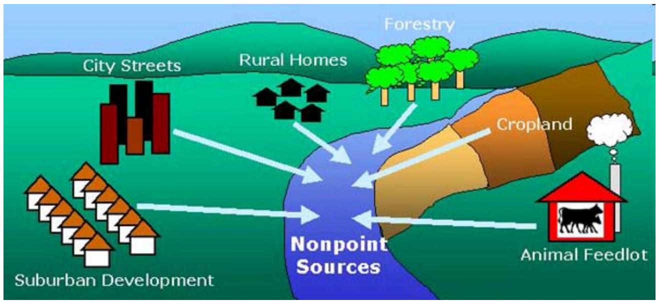


Figure 2 – Non-point pollution sources

Livestock activities can originate pollution from a number of mismanaged practices, including inadequately managed feedlots or barnyards, unprotected manure facilities and untreated wastewaters. Runoff from barnyards, feedlots, and cropland carries away manure, fertilizers, ammonia, pesticides, livestock waste, oil, toxins from farm equipment, soil, and sediment.

The identification of the pollution sources existing in a study area is very important, in order to recognize expected pollutants, a possible concentration range and to define monitoring programmes and sampling procedures. This identification can be done using tools like land cover, land use and land occupation cartography. Geographic Information Systems (GIS) can also help to determine some characteristics of the case study area, and fieldwork provides an opportunity to validate and update the data contained in the cartography.

Seasonal influences of point and non-point discharges on the pollution changes should also be considered, along with changes in flow regimes.

3 WATER QUALITY

3.1 Characterization of water bodies

All freshwater bodies are inter-connected, from the atmosphere to the sea, via the hydrological cycle. This cycle describes the continuous water movement over, inside and above earth. Water on earth is on a permanent move, altering between the liquid, vapour and solid state. The here presented parts of the hydrological cycle are considered inland freshwaters, and appear in the form of rivers, lakes or groundwater.

Rivers, streams, ponds lakes and reservoirs are generally described as surface water. These water bodies are found flowing or standing on the surface of the earth. Surface waters have origin on one of these sources (Gray, 2005):

- Surface run-off: it is generated when rain falls onto the surrounding area, flowing directly over the surface into the water body.
- Direct precipitation: rainfall that falls directly into the water body.
- Interflow: excess soil moisture that is constantly draining into the water body.
- Water table discharge: when there is an aquifer below the surface water body and the water table is high enough, the groundwater is discharged directly into the water body.

3.1.1 Rivers

Rivers are characterized by unidirectional current with a relatively high average flow velocity. The river flow is highly variable in time, depending on the climatic situation and the drainage pattern (Chapman, 1996). Generally, a river’s flow is greater in the winter than in summer, due to the larger amount of precipitation that occurs in the wet season. However, groundwater also influences the river streams. Rivers, which receive a significant amount of groundwater input, may not suffer such a drastic reduction of their stream flow in the summer after a wet winter, since aquifers are able to store great amounts of water. Even though rivers flow mostly on the surface of the land, some parts of a river course may flow underground.

The water quality of a river depends of both precipitation and geology of the catchment. Precipitation carries appreciable amounts of solid material to earth, as for instance, dust, pollen, bacterial or fungal spores. Many salts found dissolved in the rain have their origin in the sea, such as chloride, sodium, sulphate, magnesium, calcium and potassium ions. Atmospheric emissions from industry and households are also contributing material to clouds, which are then brought back to earth together with precipitation. In here, a wide range of chemicals is included, like organic solvents or nitrogen and sulphur oxides, causing acid rain. The amount and type of impurities contained in precipitation vary with location and time of year. Land use is another aspect that highly influences surface water quality, with agriculture having the most profound effect on water bodies (Gray, 2005).

The geology of a catchment also plays an important role when it comes to water quality. In general, chalk and limestone catchments result in clear hard waters, while impervious rocks, such as granite, result in turbid soft waters. These particles can have both inorganic and organic origin and make the water appear cloudy. The reason for this difference comes from the fact that rivers running in chalk and limestone areas arise as springs, or are fed from aquifers through the riverbed. As considerable amounts of water arise from groundwater, the river retains a constant clarity, flow, and temperature throughout the year, except after extended periods of rainfall. In these rivers the chemical nature is very stable, rarely altering from year to year, as the water spent a very long period in the aquifer before entering the river. During this time, water dissolves calcium and magnesium salts comprising the rock and resulting in hard water (Gray, 2005).

As soft water, rivers are usually generated by runoff from mountains the flow chemical characteristics are very close to those presented by rainfall. These rivers experience broad fluctuations in the flow regime, suffering sudden floods and droughts. Chemically these rivers are turbid due to all the silt washed into the river from superficial runoff. The content in cations, such as calcium, and magnesium, is low due to the few contact with the bedrock.

3.1.2 Lakes and reservoirs

Lakes are considered lenthic water bodies. On these water bodies, residence times are high, and may vary from one month to several hundreds of years. Lakes constantly undergo evolutionary modifications, reflecting changes that occur in the watershed they belong. It is a natural and slow process that can dramatically change as a consequence of human activities.

Many lakes undergo alternating periods of stratification, which occurs as a consequence of seasons, i.e., climate conditions (and also lake depth) regulate stratification. In temperate climates, water tends to stratify especially during summer, because water’s density changes with temperature. Water is most dense at 4ºC, expanding and becoming less dense, both above and below that temperature. Stratification also occurs in the winter, as ice covers the water surface. However, this only happens in areas where winter is very rigorous. In the springtime, as the sun heats the surface of the water and ice starts to melt, the temperature and density differences between surface and bottom water become more distinct, and lakes form two distinct layers. The top layer, or epilimnion, is warmer than the lower layer, the hypolimnion. They have different densities, and are separated by a static boundary layer, called metalimnion or thernocline, preventing the waters to mix.

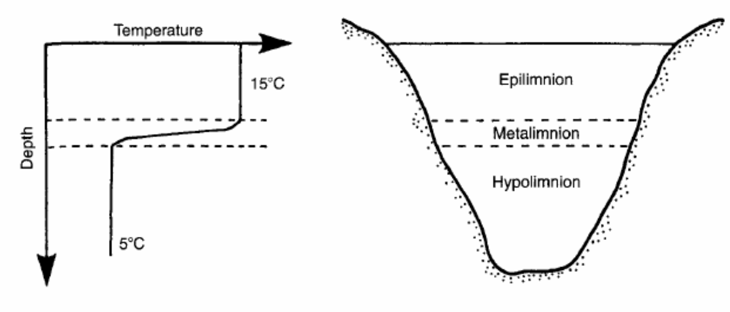


Figure 3 – Thermal stratification of lakes. Source: Gray, (2005)

The epilimnion of lakes is constantly being mixed by the wind and so the whole layer presents a warm uniform temperature, exposed to the sunlight, creating a very favorable environment for algae (Gray, 2005). Phosphorus and nitrogen are the main nutrients required for algae to grow, and are not normally present in large quantities. However, activities like agriculture generate superficial runoff, generally rich on these nutrients. When discharged into surface water this runoff represents an excess of nutrients, and massive algal growth may occur, probably resulting on algae blooms and leading to a phenomenon known as eutrophication. In the worst cases, water becomes extremely colored.

Like other plants, algae release oxygen during the day due to photosynthesis, but at night they can remove oxygen from water during respiration. When eutrophication occurs, the high amount of algae will severely deplete the oxygen concentration in the water, which may cause fish to die. In contrast, there is little mixing or movement in the hypolimnion which rapidly becomes deoxygenated and stagnant, and looses the normal aerobic biota. Dead algae and organic matter settling from the upper layers are degraded in this lower layer of the lake. As the hypolimnion has no source of oxygen to replace the amount already used, the water may become completely unprovided of oxygen. Under these anaerobic conditions, elements like iron, manganese, ammonia, phosphates and silica are released from the sediments into the water, while nitrate is reduced to nitrogen gas (Gray, 2005). On these conditions, water is not fit for its purposes, for instance like supply.

Reservoirs, on the other hand, are characterized by features that are intermediate between rivers and lakes. They can range from a small scale up to a larger scale, presenting many different, sizes and purposes, which can be water supply, irrigation, flood control or production of electrical power. A reservoir can take many years to fill, and once brought to use (especially when it comes to water supply) they should be carefully managed. This means it has to be a balance between water withdrawals and water replacing by runoff. Normally, reservoirs are filled during wintertime, when precipitation occurs in higher amounts. In the wet season, water demand is smaller than in the summer, meaning that a reservoir is able so store water during periods when water demand is minor.

The storage capacity of the reservoir is finite, which can cause either of these situations:

- In the winter, an excess of precipitation may cause the reservoir to discharge this extra water, which may cause floods downstream;
- Again in the winter, if the rainfall is not sufficient, the expected quantity of water does not occur, resulting in the reservoir not being sufficiently filed by the beginning of summer. In these circumstances, water rationing may occur.

Regarding land use around the reservoir's area, it is highly recommended its careful planning, including the activities that can and cannot be developed in the area adjacent to the water table, in order to guarantee that the water stays as clean as possible.

3.1.3 Groundwater

Geology plays an important role in topography, the development of soils, and the location and availability of groundwater. The location and characteristics depend on geology and soil properties.

The inorganic part of the earth is made up of rocks and their weathering products. A rock, by definition, contains one or more minerals. There are three fundamental classes of rocks: igneous rocks, sedimentary rocks and metamorphic rocks.

The most fundamental of these classes of rocks are igneous rocks that are formed as cooling products from the molten state. Igneous rocks are primordial in many parts of the world and are some of the world's oldest, exceeding three billion years in age. One way they can be formed is when molten rock is intruded into other rock formations and then cooled to the solid state. If the cooling is slow enough, various minerals will crystallize out into an interlocking solid mass that is characteristic of particular rocks such as granite (Delleur, 2007).

Extrusive igneous rocks like dense basalt are forced from fissures in the earth's crust and harden into vast sheets of solid material, usually containing very small crystals (due to the rapid cooling), or perhaps no crystals at all (obsidian glass). Other extrusives like lighter lava or pumice are ejected during volcanic eruptions and are highly charged with gases to form very porous and even frothy glasses resembling a sponge. Some of the ejected material may fall from the air to settle as sediment. This particular kind of deposit is known as a pyroclastic rock, that is, part igneous and part sedimentary (Delleur, 2007).

A sedimentary rock is deposited from either air or water as grains of rocks and minerals. These sediments may have been derived from the weathering of igneous, metamorphic or other sedimentary rocks. If any kind of rock, igneous, metamorphic, or sedimentary, is subjected to intense heat and pressure, such as those existing at great depths in the earth's crust, at the edge of tectonic plates, or in rising mountain ranges, the parent rock will be transformed into the third class of rock - a metamorphic rock. A metamorphic rock may contain the same chemical composition as the parent rock, but the mineral composition and structure may be changed drastically from the parent (Delleur, 2007).

Groundwater can be found in all three classes of rocks, but generally are the sedimentary rocks those that contain by far the most amounts of water due to their greater porosity.

A porous formation is formed by a set of grains and in between them exist free spaces that can be occupied by water. These voids are called pores, and porosity is defined as the volume of the pores of a rock or soil sample divided by the total volume of both pores and solid material. Porosity of a rock or soil is determined largely by the packing arrangement of its grains and the uniformity of the grain-size distribution (Delleur, 2007). More pore spaces result in higher porosity and more stored water.

A groundwater reservoir, also designated as aquifer, ca be defined as a geologic formation that has capacity to store and transmit water, and which exploration is economically cost effective. Essentially, there are two types of aquifers:

- Phreatic aquifer: permeable geologic formation partially saturated with water. It is limited in the basis by an impermeable layer and the water level in the aquifer is at the atmospheric pressure.

- Confined aquifer: permeable geologic formation totally saturated with water. It is limited on both top and bottom by impermeable layers. The water pressure in the interior of the aquifer is higher than atmospheric pressure.

This division is mainly due to the differences in the physics of flow of water in the saturated (confined aquifer) versus unsaturated zone (phreatic aquifer) (Delleur, 2007). Phreatic aquifers are recharged where the porous rock is not covered by an impermeable layer of soil, and are separated from the confined aquifer by a layer called water table, which is ahead described. Where the aquifer is overlain by an impermeable layer, no water can penetrate into the porous rock from the surface. Instead, water slowly migrates laterally from unconfined areas, forming the unconfined aquifers. There is no unsaturated zone because all porous are saturated with water, since they are below the water table level. There is also no oxygen (Gray, 2005).

If the geologic formations are not aquifers, they can be defined as:

- Aquitard: geological formation that can store water, but transmits it very slowly, making impracticable to use water from wells.

- Aquiclude: geological formation that can store water, but does not transmit it, i.e., the water does not circulate.

- Aquifuge: An impermeable body of rock that contains no interconnected openings or interstices and therefore neither absorbs nor transmits water.

Aquifers are an important source of fresh water, for example for drinking and irrigation, in many areas of the world, and are exploited by the use of wells. However, groundwater is not only abstracted directly for supply purposes but also often discharges into rivers, as either base flow or springs. This discharge may be permanent or seasonal, depending on the height of the water table within the aquifer (Gray, 2005). The water table is the top of the saturated zone, rising and falling according to the season of the year and the amount of rain and snow melt that occurs. Typically, it is higher in early spring and lower in late summer. However, heavy rainfall or drought conditions may cause changes in the typical pattern. In addition, water abstractions can disturb the natural balance of the aquifer, when they exceed the infiltration capacity. The water table can be measured by determining the level of water in boreholes and wells. The figure below shows the different types of aquifers.

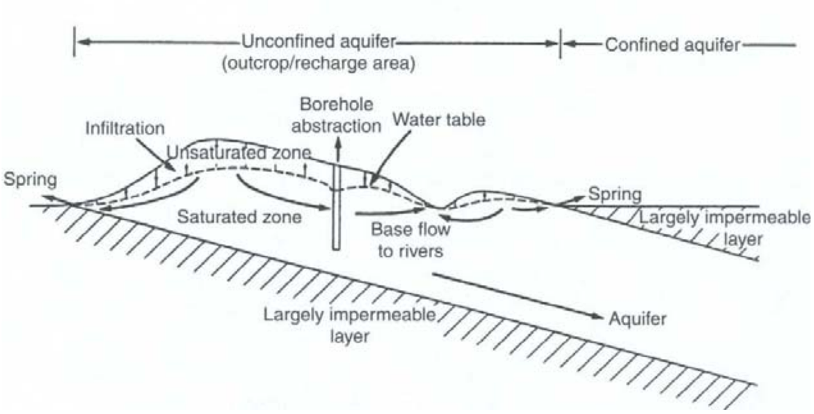


Figure 4 - Schematic diagram of groundwater systems. Source: Gray (2005).

Groundwater in phreatic aquifers is particularly vulnerable to diffuse sources of pollution, especially agricultural practices (nitrates and organic chemicals) and fallout of atmospheric pollution, arising mainly from industry. Point pollution sources, such as septic tanks, leaking sewers or farmyard drainage can also affect groundwater resources.

The unsaturated zone is the portion of the subsurface above the ground water table. The soil and rock in this zone contains air as well as water in its pores. Hydrologically, the unsaturated zone is often the main factor controlling water movement from the land surface to the aquifer, thus strongly affecting the rate of aquifer recharge, critical for the use and management of groundwater. It can be considered as a filter that not only removes undesirable substances before they affect aquifers, but also has the major effect of retarding the movement of most pollutants. This zone plays a major role mostly when major pollution incidents occur, and long periods of time can go by before the effects of, for instance, a spillage or leakage are detected in the groundwater, due to the prolonged migration period.

Groundwater quality depends of four main factors (Gray, 2005):

- The characteristics of the rain water, which can vary considerably, especially concerning acidity due to pollution and the effects of wind-blown spray from the sea, which affects coastal areas in particular.
- The characteristics of the existing groundwater.
- The characteristics of the soil through which rain water percolates.
- The nature of the rock comprising the aquifer.

Commonly, groundwater contains a number of major ions that form compounds. These are calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}), and to a slighter extent iron (Fe^{2+}) and manganese (Mn^{2+}). These are all cations that are found in water combined with an anion to form compounds sometimes referred to as salts. The major anions are carbonate (CO_3^{2-}), bicarbonate (HCO^{-}), sulphate (SO_4^{2-}) and chloride (Cl^{-}).

3.2 Definitions of water quality

The focus on water resources is often on the volume of water available for particular uses. However, it is generally recognized that water quality determines the suitability of water for a particular purpose. In order to understand this suitability, a set of selected physical, chemical and biological characteristics can be used to determine water quality. Selected characteristics are then compared to numeric standards and guidelines to decide if the water is suitable for a particular use.

Even though it may seem relatively simple, it is very hard to define water quality, mainly due to the complexity of factors that contribute to determine the quality of a given water body. Chapman (1996) proposes the following definitions to the terms:

- Quality of the aquatic environment:
    - Set of concentrations, speciation and physical partitions of inorganic or organic substances.

  - Composition and state of aquatic biota in the water body.
  - Description of temporal and spatial variations due to internal and external factors to the water body.
- Pollution of the aquatic environment: Direct or indirect introduction, by men, of substances or energy, resulting in damaging effects as:
  - Harm to living resources;
  - Hazards to human health;
  - Impediment to aquatic activities, including fishing;
  - Impairment of water quality with respect to its use in agricultural, industrial, and often economic activities;
  - Reduction of services.

The assessment of water quality (Gray, 2005) is essential for pollution control and the protection of both surface and groundwater. Water quality rarely remains static so quality data are need mainly because:

- Quality changes along time and space;
- Waste loads vary at different points in the systems;
- Allow to describe the effluent;
- Setting consents, mass balance calculations and hydrological modelling.

The main factors affecting variations in quality are dilution and water temperature that causes biological activity and oxygen solubility to change. Gray (2005) also points seasonal changes in waste inputs as a major fact influencing the quality of a given water body.

3.3 Effects of pollution on groundwater

Groundwater quality is the sum of natural and anthropogenic influences. Even though soil acts like a protection layer to groundwater, these waters have been coming increasingly polluted over the last years. It is true that many soils do have the ability to remove certain types of pollutants, including phosphorus, heavy metals, bacteria and suspended soils. However, pollutants than can dissolve themselves in water, like nitrate or ammonia, may pass through soils into groundwater and show up in alarmingly high concentrations in local drinking water wells.

Edmunds & Shand (2008) present a list of human activities that may potentially pollute groundwater and identify the main pollutants in each case. The authors also link the presented activities to the principal uses for which groundwater is needed, in order to identify the most important current and future quality issues of groundwater. A major subdivision into urban, industrial and agricultural is made, even though there is a considerable overlap between the first two. From Table 1, it is also possible to verify that some of the activities generating serious pollution risks are common to highly industrialized, newly industrializing and low development countries (mainly agricultural based economies).

Table 1 – Main activities that can potentially cause groundwater pollution. Source: Edmunds & Shand (2008)

Activity	Principal characteristics of pollution					Stage of Development			Impact of water use		
	Distribution	Category	Main types of pollutant	Relative hydraulic surcharge	Soil zone by passed	I	II	III	Drinking	Agricultural	Industrial
Urbanization											
Unsewered sanitation	U, R	P, D	p, n, o	x	yes	xxxx	xx	x	xxxx		x
Land discharge of sewage	U, R	P, D	n, s, o, p	x		x	x	x	xx	x	x
Stream discharge of sewage	U, R	P, L	n, o, p	xx	yes	x	x		xx	x	x
Sewage oxidation lagoons	U	P	o, p, n	xx	yes	x	xx	x	xx		x
Sewer leakage	U	P, L	o, p, n	x	yes			xx	x		x
Landfill, solid waste disposal	U, R	P	o, s, n, h		yes	x	xx	xxx	x		x
Highway drainage soak-away	U, R	P, L	s, o	xx	yes	x	xx	xx	xx	x	x
Wellhead contamination	U, R	P	p, n		yes	xxx	x		xxxx		
Industrial development											
Process water/effluent lagoons	U	P	o, h, s	xx	yes	x	xx	xx	xx		x
Tank and pipeline leakage	U	P	o, h	xx		x	xx	xxx	xxx		xx
Accidental spillages	U, R	P	o, h	xx	yes	x	xx	xxx	xxx		xx
Land discharge of effluent	U	P, D	o, h, s	x		x	xx	xx	x	x	x
Stream discharge of effluent	U	P, L	o, h, s	xx	yes	x	x	x	x	x	x
Landfill disposal of residues and waste	U, R	P	o, h, s		yes	x	xxx	xxx	xx		x
Well disposal of effluent	U	P	o, h, s	xx	yes		x	x	xx		x
Aerial fallout	U, R	D	a					xx	x	x	x
Agricultural development											
Cultivation with:											
Agrochemicals	R	D	n, o			x	xx	xxx	xxx	x	x
Irrigation	R	D	s, n, o	x		xx	xx	x	xxx	xxxx	x
Sludge and slurry	R	D	n, o, s			x	x	xx	xx	x	x
Wastewater irrigation	R	D	n, o, s, p	x			xx	x	xx	xx	
Livestock rearing/crop processing:											
Unlined effluent lagoons	R	P	p, n, o	x	yes	x	x	xx	x	x	
Land discharge of effluent	R	P, D	n, s, o, p	x	yes	x	x	xx	x	x	
Stream discharge of effluent	R	P, L	o, n, p	x	yes	x	x	xx	x	x	
Mining development											
Mine drainage discharge	R, U	P, L	s, h, a	xx	yes	x	xx	xx	xx	x	x
Process water/sludge lagoons	R, U	P	h, s, a	xx	yes	x	xx	xx	xx	x	x
Solid mine tailings	R, U	P	h, s, a		yes	x	xx	xx	xx	x	x
Oilfield brine disposal	R	P	s	x	yes		x	x	xx	x	x

Hydraulic disturbance	R, U	D	s		na		x	x	xx	x	x
Groundwater resource management											
Saline intrusion	U, R	D, L	s		na	x	x	xx	xxx	xxx	xx
Recovering water levels	U	D	s, o		na			x	x		x

Notes:
Distribution: U – urban, R – Rural.
Category: P – Point, D – Diffuse, L – Line.
Types of pollutant: p - Faecal pathogens; n - Nutrients; o - Organic micropollutants; h - Heavy metals; s - Salinity; a - Acidification
x to xxxx: Increasing importance or impact
na: Not applicable
Stages of development: I Low development; II Newly industrializing; III Highly industrialized

In the last decades, many countries have started to improve their investments in both water supply and sanitation programmes. Often, mainly in rural areas where small villages with few inhabitants are found, these programmes include the construction of unsewered, on-site sanitation facilities using various types of latrines. However, under certain hydrogeological conditions, unsewered sanitation can cause severe groundwater contamination by pathogenic micro-organisms and nitrate (Edmunds & Shand, 2008).

Another risk to groundwater posed by untreated wastewaters is their content of various organic compounds used in household products, like detergents and disinfectants. Unsewered sanitation consists of the installation of either septic tanks or pit latrines. There are important differences between them, regarding the risk of groundwater contamination. The next table resumes these differences, according to Edmunds & Shand (2008). The authors state that septic tanks are likely to pose a less serious threat to groundwater than pit latrines.

Table 2 – Main differences between septic tanks and pit latrines

	Septic tanks	Pit latrines
Soak-away discharge	Higher levels in the soil profile, providing more favourable conditions for pathogen elimination.	Lower levels in the soil profile.
Hydraulic loading	Likely to be less than for some pit latrines.	Likely to be higher than for some septic tanks.
Removal of solid effluent	Septic tanks are lined and their solid effluent of high nitrogen content is periodically removed.	Most pit latrines are unlined and the solid material remains in the ground.

The impact of untreated wastewater is mostly felt, according to table 1, in relation to drinking water, as these waters may contaminate groundwater supplies. Problems are usually felt only where the water table is so low that on-site sanitation systems discharge directly into the saturated zone. Even though it is know that persistent organisms may pose a risk to groundwater resources, some uncertainty still remains about the persistence in aquifers of some pathogens, mainly viruses.

The most serious problems related to sanitation generally occur on small and medium sized towns, as well as rural areas. In here, local and often untreated groundwater resources are used for water supply, meaning that the water source can experience direct pollution, either from the users, wastewaters or livestock. In larger cities the impact of unsewered sanitation may not be so significant, not only because municipal water supplies are drawn from surface water and then treated, or drawn from relatively distant well protected aquifers.

Groundwater pollution by unsewered sanitation is most likely to occur where soils are thin or absent, where fissures allow rapid movement and where the water table is shallow (Edmunds & Shand, 2008).

Landfills are the most common method of disposal of solid municipal wastes, and constitute an important potential source of groundwater pollution. Sanitary landfills are generally planned, located, designed and constructed according to a set of specifications, in order to minimize the impact on the environment, groundwater included. The construction methods adopted include lining and capping, compaction of fill and control of surface water inflow. As main threat to groundwater posed by these facilities is the leachate generated by the fill material, the design of a landfill aims to minimize leachate development by sealing the fill from rainfall, run-off and adjacent groundwater. To produce a significant quantity of leachate a flow of water through the fill is required, and the possible sources include precipitation and surface water or groundwater flowing into the landfill (Edmunds & Shand, 2008). The chemical composition of the leachate depends on the nature and age of the landfill, as well of the leaching rate. Municipal solids contain little hazardous material, yet industrial wastes may contain several toxic constituents, like metals or organic pollutants. Abandoned landfills and uncontrolled dumping can constitute an additional threat to groundwater.

Accidental pollution events from major industrial complexes also constitute a threat to groundwater. The causes of incidents include, according to Edmunds & Shand (2008), accidents during transportation, spillages due operational failures and leaks due to corrosion or structural failure of pipes or tanks. The consequence is a point source of pollution, which may be short and intense in case of an accidental spillage or small but continuous in case of a leak. However, in both cases dangerous chemicals or products may be discharged into the environment. Examples of this type of pollution include accidents during road or rail transport, for instance of industrial solvents or petroleum products. Fuel stations with buried tanks are also another example of this type of pollution, and not all the underground tanks are protected from corrosion, which may result in leakages. A major control over how the pollution develops and migrates in groundwater is strongly advised in these cases, and it should be carefully monitored, as accidental leakages will necessarily produce different plumes from those from a regular drainage infiltration.

The agricultural sector is a fundamental sector to the countries competitive economy, once it generates wealth. Still, one of the leading causes of aquifer pollution in many countries are the unsustainable agricultural practices. Modern agriculture uses a large number of chemicals, both in plant and animal production. A broad range of fertilizers, pesticides and fumigants are routinely applied to agricultural lands, thus making agriculture one of the most important sources of non point pollution. The same is true for salts and toxic trace elements, which are often a consequence of irrigation in arid and semiarid regions. While many agricultural chemicals are generally beneficial in surface soils, their leaching into the deeper vadose zone and groundwater may pose serious problems (Delleur, 2007).

The primary pollutant of groundwater is nitrate. This element moves relatively slow in soil and groundwater and it can take several years between the pollution activity and the detection of nitrate in polluting concentrations in groundwater. For this reason, it is predicted that current polluting activities will continue to affect nitrate concentration in groundwater for the next decades. The principal effects related to excessive nitrate concentration in groundwater are felt in humans. In a short term, excessive levels of nitrate in drinking water can cause serious illness (especially in children, and symptoms include shortness of breath and blueness of the skin) and sometimes death. In the long term, nitrates have the potential to cause diseases like dieresis or hemorrhaging of the spleen, due to lifetime exposure to values higher that maximum contaminant value.

Pesticides applied in agricultural land can also leachate to the underlying groundwater. Even though the use of organo-chloride insecticides is now banned or rigorously controlled, new compounds are continually being introduced. They all are manufactured to be toxic and persistent, and even a small percentage of an applied pesticide could be enough persistent and mobile to reach the groundwater systems (Edmunds & Shand, 2008). The authors point hydrological environments with shallow water tables and coarse textured soils low in organic matter (including coastal and island limestone, sands and some alluvial deposits) as the more likely to be most vulnerable to the leaching of pesticides.

Another form of groundwater pollution deriving from agricultural activities is salinity, resulting from low irrigation efficiency practices and lack of proper drainage measures. Over irrigation without adequate drainage can cause groundwater levels to rise, resulting in both soil and groundwater salinisation from direct phreatic evapotranspiration. Preventing the problem of groundwater salinity requires efficient irrigation, combined with effective drainage and appliance of best management practices.

Animal production has also been using an increasing variety of pharmaceuticals and hormones, many of which are being released into the environment through animal waste, along with pathogenic microorganisms. According to Delleur (2007), potential problems about the presence of this pharmaceuticals and hormones in the environment include:

- Abnormal physiological processes and reproductive impairment;
- Increased incidence of cancer;
- Development of antibiotic resistant bacteria;
- Increase toxicity of chemical mixtures.

As agriculture seems to pose the major threat to groundwater, it is important to develop Best Management Practices and create associations that work directly with farmers, in order to develop management plans that restrict fertilizer applications to periods of active plant growth, which will help prevent groundwater pollution, once nitrate is directly absorbed by growing vegetation. Fertilizers should not be applied during or before rainy periods, so it is recommended a previous knowledge of the weather forecast.

Mining activities can also be associated to groundwater pollution. The nature of pollution depends on the materials being extracted and the post extraction processing. The major pollutants are, according to Edmunds & Shand (2008) coal, salt, potash, phosphate and uranium mines. Metalliferous mineral extraction is also important, but stone, sand and gravel quarries, although more numerous and widespread, are less chemically important. At most surface or underground mines, groundwater will flow into excavated areas and must then be pumped out in order to dewater places where mining activities are intended to take place. The pumped water may have a high content in minerals, and its usual characteristics include low pH (down to 3) and high values of iron, aluminium and sulphate. The disposal of this type of effluents to both surface and groundwater can cause serious impacts on water quality for all uses. Additionally, groundwater quality may be affected by other factors, like for instance, the handling, storage, and disposal of mining wastes, the mine excavation itself or the storage and handling of chemicals, reagents, and fuels.

4 European Legal Framework

The need to protect the European Union waters has been highlighted for more than two decades. Regarding groundwater in particular, its protection regimes and associated policies have suffered from a lack of overall planning and specific instruments that could ensure concerted actions across the EU. Early groundwater legislation (Directive 80/68/EEC, on the protection of groundwater against pollution caused by certain dangerous substances) rather narrowly focused on control of emissions of substances from industrial and urban sources (Edmunds & Shand, 2008).

Requirements for control of diffuse sources also came afterward in the legislative framework, particularly with the introduction of Nitrates Directive (Directive 96/676/CE, concerning the protection of waters against pollution caused by nitrates from agricultural sources) and IPPC Directive (Directive 61/96/EC, on integrated pollution prevention and control).

However, the major step towards an integrated management of the water resources inside the community space was taken with the Water Framework Directive (Directive 2000/60/EC of the European Parliament and of the Council, establishing a framework for the Community action in the field of water policy). WFD introduces an integrated approach, focused on protection measurements and it requires governments to take a new holistic approach to managing their waters.

In this context, and for the first time, groundwater has become a part of an integrated water management system, as they are included in WFD's river basin management planning. Milestones considering delineation of groundwater bodies, economic analysis, characterization of pressures and impacts, monitoring and design of programmes of measures are clearly defined, aiming to achieve good quantitative and chemical status for all groundwater bodies by the end of 2015.

The difficulty of defining clear criteria concerning groundwater chemical status has led the European Parliament and Council to include provisions in the WFD, in the Article 17, asking the Commission to come forward with a "Daughter Directive", providing additional technical information. Discussions begun in 2001, and involved policy makers from the member states, different stakeholders and the scientific community. As a result, the Directive 2006/188/EC on the protection of groundwater against pollution and deterioration was adopted on 12 December 2006 (Edmunds & Shand, 2008).

4.1 Water Framework Directive

The Water Framework Directive (2000/60/CE) is the most substantial piece of water legislation ever produced by the European Commission, providing the major driver for achieving sustainable management of water in the Member States for many years to come. The overall aim of the Water Framework Directive (WFD) is to establish a framework for the protection and management of surface waters, including estuaries, coastal waters and groundwater in the EU.

According to the WFD, water is not a commercial product like any other but, rather, a heritage that must be protected, defended and treated as such. As so, it requires that all inland and coastal waters within defined river basin districts must reach at least good status, at the latest, 15 years after the Directive is published (and that this status does not deteriorate in any waters) and defines how this should be achieved through the establishment of environmental objectives and ecological targets for waters. The Directive's environmental objectives are described on Article 4:

- Implementation of the necessary measures to prevent deterioration of the status of all water bodies.
- Protection, enhancement and restoration of all bodies of water, with the aim of achieving good surface water status at the latest 15 years after the date of entry into force of the Directive.
- Protection and enhancement of all artificial and heavily modified bodies of water, with the aim of achieving good ecological potential and good surface water chemical status at the latest 15 years after the date of entry into force of the Directive.
- Progressive reduction of pollution from priority substances and ceasing or phasing out emissions, discharges and losses of priority hazardous substances.
- Protection, enhancement and restoration of all groundwater bodies, ensuring a balance between abstraction and recharge of groundwater, with the aim of achieving a good groundwater status at the latest 15 years after the date of entry of force of the Directive.
- Implementation of measures necessary to reverse any significant and sustained upward trend in the concentration of any pollutant resulting from the impact of human activity in order progressively to reduce pollution of groundwater.

In essence, the Framework Directive aims to prevent pollution at source and sets out control mechanisms to ensure that all pollution sources are managed in a sustainable way. It protects groundwater and sets ambitious objectives for its quality and quantity. For the aquatic ecosystems of our rivers, lakes and coastal waters, ambitious ecological objectives are also set. Although today much of Europe's groundwater and surface waters are polluted, they should all reach "good status" by the year 2015 (European Commission, 2002). All these objectives must be integrated for each river basin.

The "good status" is applied to all surface waters, and requires that both "good chemical status" and "good ecological status" or "good ecological potential" (the latter referring to heavily modified or an artificial body of water) are achieved. For groundwater, "good status" means the status achieved by a groundwater body when both its quantitative status and its chemical status are at least good.

Concerning surface water, "chemical status" is related to the presence of chemical substances in the water, which would not occur in natural conditions. These substances are susceptible of causing damages not only in the water environment but also to human health, flora and fauna, as a result of their persistency, toxicity and bioaccumulation. Among these, are the dangerous substances defined by the List I of the Directive 76/464/EEC on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community (Henriques *et al.*, 2000). For surface water, "good chemical status" is achieved by the waters where the referred pollutants are not present, or where their concentration does not exceed the environmental quality standards established at Community level.

The concepts "ecological status" and "ecological potential" are defined by the physical, chemical and biological conditions of the water (Pio & Henriques, 2000).

"Ecological status" is an expression of the quality of the structure and functioning of aquatic ecosystems associated with surface waters (European Union, 2000). It embraces several parameters related to the physical-chemical nature of the waters, to the hydrodynamic characteristics and the physical structure of the waters, being important those related to the conditions of the biotic elements of the ecosystems (Pio & Henriques, 2000).

The "good ecological status" is the main goal fixed by the WFD for the surface waters in the Community. It is defined as the state of a surface water body that, even though may present a deviation when compared to the "reference situation", resulting from significant human activity influence, still is an rich, varied and sustainable ecosystem. The “reference situation” is the state that would be achieve, in the limit, if all human influence over the water would stop.

The “ecological potential” is applied to the bodies of surface water, which characteristics have changed due to human activities, resulting on substantial change relatively to the type of the reference water body.

It is in the physical space of the river basin that changes resulting from pressures, caused mainly by human activities are felt, and where water quality and quantity issues should be addressed. It is also inside the river basin that management and planning measures should be defined. In the river basin are also implemented monitoring programs, required by the WFD, to examine coherently and comprehensively the state of the water bodies. The monitoring is also a tool to support decision making in the water resources management. In this context, it makes sense to use water quality indexes that, through succinct information, allow analyzing the possible deterioration of water resources, both along the basin and over time (Toledo & Nicolella, 2002).

In order to understand the current status of the waters and to define measures to achieve the goals imposed by WFD, it’s essential to develop a monitoring programme, also foreseen in the Directive. The directive sets a five-class scale - high, good, moderate, poor and bad status - and it requires Member States to achieve good status in all waters by 2015. Article 8 of the WFD sets out the monitoring requirements for the monitoring of surface water status, groundwater status and protected areas, which “are required to establish a coherent and comprehensive overview of water status within each river basin district.” Monitoring will provide the information needed to assess the state of the water environment, to manage pressures on the water environment and to assess long term trends.

For surface water, the programmes referred in WFD should cover the volume and level or rate of flow to the extent relevant for ecological and chemical status and ecological potential, and the ecological and chemical status and ecological potential. For groundwater, such programmes shall cover monitoring of the chemical and quantitative status. Concerning protected areas, the programmes shall be supplemented by those specifications contained in Community legislation under which the individual protected areas have been established. Once Member States have determined the current status of their water bodies, monitoring then helps Member States to track the effectiveness of measures needed to clean up water bodies and achieve good status.

WFD specifies three types of monitoring (European Commission, 2008):

- Long term surveillance monitoring: provides a broad understanding of the health of water bodies and tracks slow changes in trends, such as those resulting from climate change.
- Operational monitoring: focuses on water bodies which do not meet good status and on the main pressures they face – pollution where this is the main problem, water flow where extraction creates risks. This type of monitoring tracks the effectiveness of investments and other measures taken to improve the status of water bodies.
- Investigative monitoring: when needed further information about surface water bodies that cannot be obtained via operational monitoring, including information on accidents.

In addition to these three main types of monitoring, Member States need to carry out more detailed analysis in areas that are protected for drinking water or for natural habitats and species.

4.2 Nitrates Directive

European agricultural practices have been focused on maximizing the production, which has tended to result in the adoption of intensive production methods. Even though this policy has been quite successful in achieving increased production, has brought about vast amount of negative effects on the environment. Intensive agricultural production has inevitably resulted in the increased use of chemical fertilizers, and more significantly large numbers of livestock were enforced to be concentrated on small areas of land. In some regions of the EU, intensive livestock production has led to a structural excess of the quantities of manure produced. In other words, land has been deposited with the amount of manure that cannot be disposed of without causing grave nitrate pollution.

Aiming to reduce water pollution caused by nitrates from agricultural sources, as well as with the intention of preventing further uncontrolled application of nitrates into soils, the European Council adopted the Directive 91/676/EEC in 1991, concerning the protection of water against pollution caused by nitrates from agricultural sources.

Member States must identify waters affected by such pollution and waters which could be affected by such pollution and designate them and all known areas draining into those waters as 'vulnerable zones'. The

Nitrates Directive requires Member States to monitor surface waters and groundwater for nitrate pollution against a maximum limit of 50 mg NO_3/l. For these zones they must then establish and implement action programmes to reduce pollution. Such action programmes contain mandatory measures including maximum amounts of manure that can be applied to land every year. Action programme measures are required to promote best practices in the use and storage of fertiliser and manure by four key measures:

- Limiting inorganic nitrogen fertiliser application to crop requirements;
- Limiting organic manure applications;
- Seasonal restrictions on the application of slurry, manure sand sludge on sandy and shallow soils;
- Maintenance of farm records that encompass cropping, livestock numbers and fertiliser management.

For areas outside the vulnerable zones reduction of pollution has to be promoted by voluntary codes of good agricultural practice. Member States are in this context obliged to monitor the nitrate concentrations in groundwater and surface waters as well as eutrophication in surface waters.

However, Member States may be exempted from the obligation to designate specific vulnerable zones if they set up an action programme for their entire national territory. These action programmes must impose restrictions as to when and how much fertiliser may be used, determine minimum storage capacities for manure, and contain provisions relating to fertiliser application on steep sloping grounds and alongside watercourses.

4.3 Directive on the protection of groundwater

The Directive 2006/188/EC on the protection of groundwater against pollution and deterioration establishes specific measures to prevent and control groundwater pollution. This directive sets up criteria for the assessment of good groundwater chemical status and for the identification and reversal of significant and sustained upward trends, as well as for the definition of starting points for trend reversals. These criteria take into account local characteristics and allow further improvements to be made based on monitoring data and new scientific knowledge.

The groundwater directive complements WFD and it requires:

- The establishment of groundwater quality standards by the end of 2008;
- The development of pollution trend studies using existing data, which is mandatory by WFD;
- The achievement of WFD’s environmental objectives by 2015, through reversion of pollution trends and implementation of measures to limit or prevent inputs of pollutants into groundwater;
- The review of technical provisions of the directive in 2013 and every six years thereafter;
- Compliance with good chemical status criteria, based on EU standards of nitrates and pesticides and threshold values established by Member States.

This Directive establishes threshold values for the pollutants, groups of pollutants and indicators of pollution which, if exceeded, will indicate that a given groundwater body is at risk. As a minimum, Member States must establish threshold values for: ammonium, arsenic, cadmium, chloride, lead, mercury, sulphate, trichloroethylene and tetrachloroethylene.

However, the concept of “environmental quality” of groundwater is understood differently from country to country, and from various sector perspectives. In other words, the distinction between the natural environmental quality and the quality of groundwater for specific uses (mainly drinking water, but also irrigation, animal watering and industrial uses) was never clearly made. Mainly, it was due to the fact that little is known about what is meant by “natural environmental quality” for groundwater, underlying the need for research in this field in order to understand better groundwater environmental mechanisms and to provide knowledge for its better management (Edmunds & Shand, 2008).

Knowledge about “natural quality” of groundwater is yet scarce, and the on-going exchanges among scientific and policymaking communities are needed to adopt a more detailed common methodology for the definition of groundwater threshold values and to put it into practice (Edmunds & Shand, 2008). Still, considerable developments in groundwater management are expected in the next years, also including better interactions among policy, science, public and other stakeholders. This, together with an improved data production and knowledge should allow a great progress towards a better understanding of groundwater systems.

5 Guidelines to Plan a Groundwater Monitoring Programme

Many countries are now undertaking water and soil management policies aiming to achieve a sustainable use of their resources, as well as an effective protection of their quality. In order to understand the state of the environment it is necessary to resort to the available monitoring tools which, when correctly used, will provide an accurate overview of the pollutants present in a given area.

Water and soil monitoring is a complex undertaking. Cost-effective monitoring relies on careful planning and critical reading of the scientific literature. These activities will ensure that the choice of sampling points and analytical procedures result in the collection of high quality data. The information needs of each program must be recognized and all subsequent monitoring network design and operation decisions must be made considering the available data. In this sense, monitoring is an evolutionary process that should be refined as the base information expands (Barcelona *et al.*, 1985).

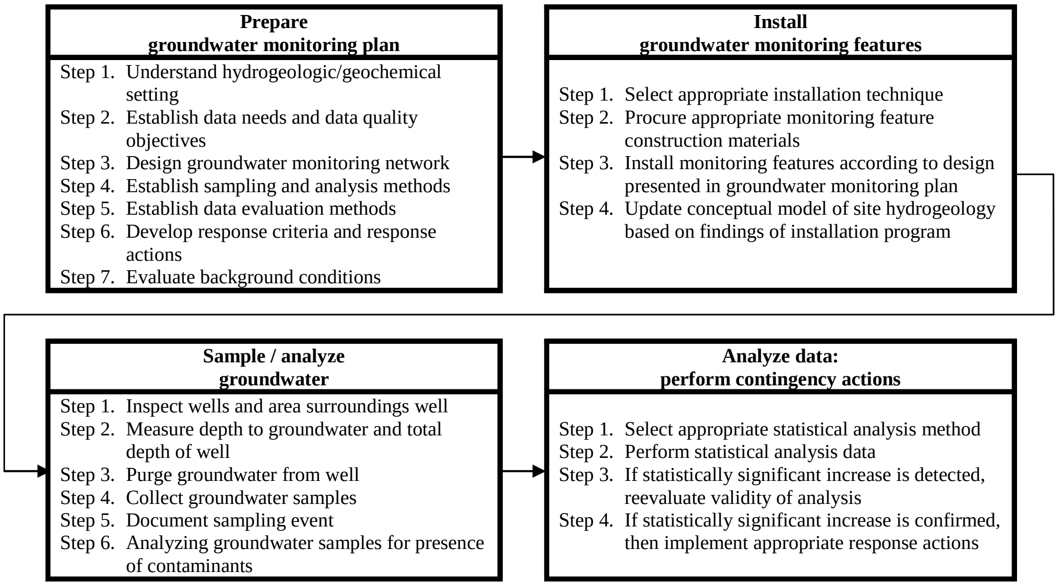
The objectives of environmental sampling and analysis may vary depending on the specific project, including regulatory enforcement, regulatory compliance, routine monitoring, emergency response, and scientific research (Zhang, 2007). The examples are as follows:

- To determine how much pollutant goes into environment through stack emission, wastewater discharge, or other sources, in order to comply with a regulatory requirement.
- To measure ambient background concentration and assess the degree of pollution and to identify both short and long term trends.
- To detect accidental releases and evaluate the risk and toxicity to both human and biota.
- To study the fate and transport of contaminants and evaluate the efficiency of remediation systems.

The field work associated with the collection and transport of samples will account for a substantial proportion of the total cost of a monitoring programme. Sampling expeditions should, therefore, be planned and carried out in such a way that efforts are not wasted. If, for example, an essential piece of equipment is forgotten or an inadequately described sampling station cannot be found, the value of that particular sampling expedition is seriously compromised. Similarly, if unrealistic estimates of travel time are made and an expedition takes longer than intended, samples may be held longer than the maximum allowable storage time and the results of analyses will be of questionable value. Having this, the sample collection process should be coordinated with the laboratory so that analysts know how many samples will be arriving, the approximate time of their arrival and the analyses that are to be carried out, in order to previously prepare the material needed to perform the analysis (UNEP/WHO, 1996).

5.1 General considerations

Groundwater is used for a variety of purposes, including irrigation, drinking water supply and manufacturing. In parallel, groundwater is also the source of a large percentage of surface water. To verify that groundwater is suited for its use, it is necessary to proceed to a quality assessment, by collecting samples for subsequent analysis. These samples should be collected according to a monitoring plan, in order to give an accurate overview of the system being monitored. The Figure 5, (Delleur, 2007) shows a flow diagram with the typical sequence of groundwater monitoring activities.



Prepare groundwater monitoring plan

Step 1. Understand hydrogeologic/geochemical setting
Step 2. Establish data needs and data quality objectives
Step 3. Design groundwater monitoring network
Step 4. Establish sampling and analysis methods
Step 5. Establish data evaluation methods
Step 6. Develop response criteria and response actions
Step 7. Evaluate background conditions

Install groundwater monitoring features

Step 1. Select appropriate installation technique
Step 2. Procure appropriate monitoring feature construction materials
Step 3. Install monitoring features according to design presented in groundwater monitoring plan
Step 4. Update conceptual model of site hydrogeology based on findings of installation program

Sample / analyze groundwater

Step 1. Inspect wells and area surroundings well
Step 2. Measure depth to groundwater and total depth of well
Step 3. Purge groundwater from well
Step 4. Collect groundwater samples
Step 5. Document sampling event
Step 6. Analyzing groundwater samples for presence of contaminants

Analyze data: perform contingency actions

Step 1. Select appropriate statistical analysis method
Step 2. Perform statistical analysis data
Step 3. If statistically significant increase is detected, reevaluate validity of analysis
Step 4. If statistically significant increase is confirmed, then implement appropriate response actions

Figure 5 – Steps to define a groundwater monitoring plan. Source: Delleur (2007)

Developing a groundwater monitoring plan requires an in-depth understanding of site conditions, contaminant properties, regulatory requirements, and other technical considerations. An understanding of the factors that could affect the quality, validity or representativeness of samples is also essential.

Regarding the development of a monitoring plan, it is recommended a step by step approach, as it helps to minimize errors, and provides a clear and concise strategy for identify the goals, requirements, and limitations of the program. These plans ought to be able not only to describe each and every aspect of the groundwater monitoring but also to control monitoring activities in order to guarantee that the overall goals of the groundwater monitoring strategy are fulfilled. A comprehensive and effective groundwater monitoring plan should address each activity that will occur during sampling analysis, data interpretation and response actions to be taken based on the results of monitoring (Delleur, 2007).

The preparation of a groundwater monitoring plan begins with the understanding of the hydrogeological/geochemical setting. This knowledge is an essential prerequisite to design an effective groundwater system. This first information can be attained from available data from site explorations, literature reviews and previous experience with similar sites. It is also important to review any previous studies done about the area. Regarding groundwater, data that should be collected include, among others, aquifer hydrogeological parameters, like transmissivity or storage properties (i.e., specific yield or specific capacity). It is also essential to have a geologic characterization of the site, as it is necessary to understand the travel paths contaminants would take if they were introduced into groundwater. Delleur (2007) refers some examples of information that should be obtained before installing groundwater monitoring features:

- both horizontal and vertical limits of the aquifers and of confining units or aquitards,
- presence of interconnections between aquifers,
- anisotropies in aquifer material, presence of discontinuities (e.g., fractures, solution cavities, channel deposits, etc.) within or between stratigraphic units,
- gradual variations of the stratigraphic units with depth or with horizontal location, and
- the nature of the earth materials within the aquifers (e.g., particle size, angularity, dispersion-related properties, etc.).

The surface of topography of the site is another important piece of information that may provide an indication of the potential impact of a contaminant release to groundwater, and also of the path these contaminants took until reaching an aquifer after being released to ground surface. The interconnection between surface water and groundwater is another interesting issue of knowledge, as well as aspects of site's lithology, as it may give clues about the mechanisms that control groundwater flow and, consequently, contaminant transport.

5.2 Monitoring objectives

Naturally occurring groundwater have become increasingly impacted by human influences, emphasizing the need to develop methodologies for identifying and recognizing not only their natural characteristics, but also the extend of an eventual pollution event, as a basis of a correct water resources management.

Groundwater is an important part of the hydrological cycle and it is mainly recharged by the water that precipitates and infiltrates through soil. As soil functions act as a protective layer to this type of waters, they are generally less vulnerable to pollution events. However, once polluted, it is more difficult to recover an aquifer than a river or a lake.

The purpose of groundwater monitoring is to define its physical, chemical and biological characteristics. If the groundwater does not meet the requirements of its intended use, or if it could be harmful to human health or the environment, it may need to be remediated. It is also emphasized that the purpose of a groundwater monitoring program should be defined before monitoring begins so that appropriate procedures, techniques, and analyses can be planned that will meet the specific needs of the project. There are four types of groundwater monitoring programs (Delleur, 2007):

- Detection monitoring programs: used to detect the impact of pressures on groundwater quality.
- Assessment monitoring programs: used not only to assess the nature and extent of contaminants that have been detected in groundwater, but also to collect data that may be needed to perform a design for remediation of the groundwater.
- Corrective action monitoring programs: used to assess the impact of a groundwater remediation on contaminant concentrations as a tool in evaluating the success of this type of action.
- Performance monitoring programs: used to evaluate the effectiveness of an element of a groundwater remediation system in meeting the design criteria for that element.

A groundwater monitoring programme should include the following steps (Leitão *et al.*, 2008):

- Physical-chemical parameters and type of pollutants to analyze;
- Places to monitor (monitoring points density, localization and type of infra-structure);

- Monitoring frequency;
- Monitoring techniques, methods and required equipment.

5.3 Selection of parameters to analyze

Ideally we would like to monitor “pollution”. The problem is that such parameters are so many and diverse that they are beyond the capability of any one monitoring system. Furthermore we are restricted by the sensors that are available, their overall performance in the field and the funding available for the project.

Monitoring programmes are generally designed in order to give response to a predefined purpose. Some common objectives of these programs include the determination of whether concentrations of specific chemical constituents are within the legal values or the measurement of the effectiveness of management measures implemented in order to protect the water resource. Still, in both cases it is necessary to proceed to a previous selection of which parameters will be analyzed.

Parameter selection for chemical measurements is very important to the effective planning of both sampling and analytical protocols. For exploratory efforts, it is useful to obtain slightly more chemical and hydrologic data than those required by the immediate information needs of the program. The added data can normally be put to good use as the site conditions become better defined. For example, in a situation where essentially no chemical data exists for a site, a complete mineral analysis should be included. The results provide an internal consistency check on major ionic constituents, field determinations and the potential effects of unusually high levels of metals or nutrient anions. The results of the complete mineral analysis and field determinations define the major ion solution chemistry, which is quite valuable to obtaining an overall picture of the subsurface system of interest (Barcelona *et al.*, 1985).

Having a complete mineral analysis and a clear view of information needs, it is possible to select any additional chemical parameters of interest. These parameters may be characterized as general groundwater quality parameters, pollution indicator parameters, and specific chemical constituents.

The process of selecting parameters should also consider eventual pollution sources present on the study area. Land use should be used to support this choice, as for instance, pollutants found in agricultural areas will necessary be different from those found in industrial or urbanized areas.

Table 3 contains an example of parameters that can be analyzed in groundwater sampling, as the final group should always be defined according to the above described. Regardless the amount of base information, the planning effort must incorporate flexibility to meet a variety of contingencies. The basis of a successful monitoring program is a robust, integral sampling protocol, coupled with proven analytical schemes. The next paragraphs briefly explain the parameters presented in Table 3.

Measuring the groundwater level is important to determine the hydrological regime of the aquifer, and must be measured at the time and place of water sampling.

Water bodies experience temperature changes along with normal climate fluctuations. These variations have a seasonal pattern. Groundwater usually maintains a quite constant temperature, normally close to the mean annual air temperature, in case of superficial aquifers. However, deep aquifers have higher temperatures due to the earth's thermal gradient. Temperature should be measured in situ and recorded at the same time of water sampling collection. This parameter should always be included in sampling programmes.

The pH is an important variable in water quality assessments, as it influences several biological and chemical processes within a water body. The pH is a measure of the acid balance of a solution and is scale from 0 to 14 (very acid to very alkaline). Neutral conditions are represented by a pH equal to 7. Ideally, pH should be determined in situ, so the many natural factors can influence it. As a temperature dependent parameter, water temperature must also be measured in order to accurately determine the pH.

Table 3 - Example of groundwater parameters to include on chemical analyses. Source: Leitão *et al.,* 2008.

Measure in situ	*Chemical Analysis*	
Temperature	Total Organic Carbon	Cadmium
pH	Biochemical Oxygen Demand	Chromium
Redox Potential	Chemical Oxygen Demand	Lead
Electric Conductivity	Nitrate	Copper
Dissolved Oxygen	Total Phosphorus	Zinc
	Anions: Chloride, bicarbonate, sulphate	Iron
	Cations: Calcium, magnesium, sodium, potassium, manganese	

The redox potential characterizes the oxidation–reduction state of natural waters. Ions of the same element but with different oxidation states form the redox system that is characterized by a certain value. The co-existence of a number of such systems leads to an equilibrium that determines the redox state of the water.

This parameter can be measured in situ. For groundwater, it is recommended that redox potential is measured "in-line" in the flowing discharge of a pump (Edmunds & Shand, 2008).

Electric conductivity is defined as the capacity that water has to conduct electrical current. It is sensitive to variations in dissolved solids, mostly mineral salts. The degree to which these dissociate into ions, the amount of electrical charge on each ion, ion mobility and temperature all have an influence on conductivity (Edmunds & Shand, 2008). Generally, this parameter is measured in situ, and can also be continuously measured and recorded.

Oxygen is essential to all forms of aquatic life, including those organisms responsible for the self purification processes in natural waters. Even though dissolved oxygen is of limited use as an indicator of pollution in groundwater, measuring this parameter is critical to the scientific understanding of the potential for chemical and biochemical processes in groundwater. Organic matter or oxidable minerals present in some aquifers rapidly deplete the dissolved oxygen. Therefore, in aquifers where organic materials are less plentiful, groundwater containing measurable concentrations of dissolved oxygen can be found (Edmunds & Shand, 2008).

Most freshwaters contain organic matter, which can be measured as total organic carbon. For indicative purposes, an clue about the amount of organic matter present can be obtained by measuring related properties, as the biochemical oxygen demand or the chemical oxygen demand. In most samples the following relation is true:

- Chemical Oxygen Demand > Biochemical Oxygen Demand > Total Organic Carbon

However, in some situations this relationship may not be true, such as when the sample contains toxic substances (Edmunds & Shand, 2008).

Organic matter in groundwater plays an important role in controlling geochemical processes by acting as a proton donor/acceptor and as pH buffer, by affecting the transport and degradation of pollutants, and by participating in mineral dissolution/precipitation reactions. Dissolved and particulate organic matter may also influence the availability of nutrients and serve as a carbon substrate for microbial mediated reactions. Natural organic matter plays an important role in the mobilization of hydrophobic organic species, metals, and radionuclides. Many contaminants virtually immobile in aqueous systems can interact with dissolved organic carbon or colloidal organic matter, resulting in migration of hydrophobic chemicals. Although organic matter is often present in low concentrations in subsurface systems, this organic matter can exhibit significant reactivity with contaminants.

The chemical oxygen demand is a measure of the oxygen equivalent of the organic matter in a water sample that is susceptible to oxidation by a strong chemical oxidant. It is widely used as a measure of the susceptibility to oxidation of the organic and inorganic materials present in water bodies and the effluents from sewage and industrial plants (Edmunds & Shand, 2008).

The biochemical oxygen demand is defined by the amount of oxygen required for the aerobic microorganisms present in the sample to oxidize the organic matter to a stable inorganic form. Standard procedures used to determine this parameter measure the amount of oxygen consumed after incubating the sample in the dark, generally at a temperature of 20°C during a specific period of time, usually five days. The oxygen consumption is determined by calculating the difference between the oxygen concentrations in the sample before and after the incubation period.

The hardness of natural water depends mainly on the presence of dissolved both calcium and magnesium salts. The total content of these salts is known as general hardness, which can be further divided into carbonate hardness (determined by concentrations of calcium and magnesium hydrocarbonates), and non-carbonate hardness (determined by calcium and magnesium salts of strong acids). Hydrocarbonates are transformed during the boiling of water into carbonates, which usually precipitate Carbonate hardness is also known as temporary, whereas the hardness remaining in the water after boiling is called constant (Edmunds & Shand, 2008). Water hardness in most groundwater is naturally occurring from weathering of limestone, sedimentary rock and calcium bearing minerals. Hardness can also occur locally in groundwater, resulting from chemical and mining industry effluent or excessive application of lime to the soil in agricultural areas.

The nitrate ion is the common form of combined nitrogen found in natural waters. It may be reduced to nitrite by denitrification processes under anaerobic conditions. Even though nitrate is a common nitrogenous compound to be found in natural waters due to normal processes of the nitrogen cycle, anthropogenic sources have greatly increased the nitrate concentration groundwater. The largest anthropogenic sources are agricultural activities, as a result of application of nitrogen fertilizers and septic tanks.

Phosphorus is a naturally occurring element that exists in minerals, soil, living organisms and water. Plant growth and development requires phosphorus, like nitrogen, in large amounts. Phosphorus is essential for early root development and hastens plant maturity, and when its level is below what plants need it can be supplied to the soil by the addition of fertilizers or organic residuals (e.g. manure). However, high application rates of these fertilizers can result in a phosphorus accumulation in soil. This phosphorus is then subject to leaching loss or transport in surface runoff either in soluble or in particulate forms. Phosphorus that is moving downward in the soil profile can eventually reach the groundwater.

Chloride is an element found in most common salts, such as road salt, table salt and water-softener salt. Chloride is a very soluble element, naturally present in groundwater, particularly in deep bedrock aquifers. This chloride is a remnant of the seawater present at the time rocks were formed. Chloride in groundwater can also have its origin in human activities, like septic tank leachate, as a result of water softening or other activities in the household, or leaching from road’s de-icing salts. In coastal areas groundwater supplies become high in chloride if pumping exceeds the recharge, causing salt water to intrude into the fresh water aquifer. Chloride levels can also be elevated naturally by flow of groundwater through areas with natural salt deposits.

Sulphate in groundwater can be derived from atmospheric deposition of oceanic aerosols and leaching of sulphur compounds, either sulphate minerals such as gypsum or sulphite minerals such as pyrite, from sedimentary rocks. Human sources include leachate from landfills and agricultural sources.

Calcium is present in groundwater, and is readily dissolved from rocks rich in calcium minerals, particularly carbonates and sulphates, essentially limestone and gypsum. Calcium occurs in waters in the form of bicarbonate and its solubility depends on the quantity of dissolved carbon dioxide. The amount of dissolved carbon dioxide depends on temperature and pressure, meaning that these factors determine the solubility of calcium bicarbonate. Every changes in both temperature and pressure resulting in modifications of the content in carbon dioxide will be reflected on the amount of calcium. In groundwater, these changes result in either solubilisation or precipitation of the calcium carbonate.

Magnesium is an element with a geochemical behaviour very similar to calcium. However, contrary to calcium, it forms more soluble salts. Magnesium arises mostly from the weathering of rocks containing ferromagnesian minerals and from some carbonate rocks.

Sodium is one of the most abundant elements on earth. Sodium salts are highly water soluble and all natural waters contain sodium. Regarding groundwater, the presence of sodium is because nearly all rocks and soils contain sodium compounds from which sodium is easily dissolved. The most common sources that may increase sodium levels in groundwater are:

- Erosion of salt deposits and sodium bearing rock minerals;
- Naturally occurring brackish water of some aquifers;
- Salt water intrusion into wells in coastal areas;
- Infiltration of surface water contaminated by road salt;
- Irrigation and precipitation leaching through soils high in sodium;
- Groundwater pollution by sewage effluent;
- Infiltration of leachate from landfills or industrial sites.

Generally sodium is measured when the water is used for drinking or agricultural purposes, particularly irrigation. Excessive sodium ions on certain soil types were found to deteriorate soil structure and impair soil drainage and also to increase runoff and erosion. The parameter “sodium adsorption ratio” is used to evaluate the risk of soil sodification and therefore to assess whether water is suitable for irrigation. This ratio estimates the degree to which sodium will be adsorbed by the soil. Higher values imply that the sodium present in the irrigation water may replace the calcium and magnesium ions in the soil, potentially causing damage to the soil structure (Edmunds & Shand, 2008). For irrigation waters, sodium adsorption ratio can be defined as follows,

$$SAR = \frac{Na^{+}}{\sqrt{\left(Ca^{2+} + Mg^{2+}\right)/2}} \qquad (1)$$

Where the concentrations of sodium, magnesium and calcium are expressed in milliequivalents per litre (meq/l).

Potassium is an abundant chemical element in the Earth’s surface. However, once it is easily fixed by clay and highly used by plants, potassium is found in low concentrations in natural groundwater. Another reason is because rocks that contain potassium are relatively resistant to weathering. The main sources of potassium in groundwater are agricultural practices, due to the application of fertilizers, and leachate from landfills.

In groundwater, the most common sources of manganese are naturally occurring, for example from weathering of manganese bearing minerals and rocks. Industrial effluent, acid-mine drainage, sewage and landfill leachate may also contribute to increase manganese contents in local groundwater.

Generally, trace amounts of metals are always present in freshwaters from the weathering of rocks and soils. However, when in high concentrations, heavy metals are priority toxic pollutants that severely limit the beneficial use of water for domestic or industrial application. Some trace elements, such as manganese, copper and zinc are necessary in low concentrations for all living organisms. The same metals, however, discharged into natural waters at increased concentrations in sewage, industrial effluents or from mining operations can have severe toxicological effects on humans and the aquatic ecosystem. Significant amounts of heavy metals also enter groundwater due to atmospheric deposition. Lead, for instance, is still widely used as an additive in petroleum for automobiles and is emitted to the atmosphere in their exhaust gases, thereby entering the hydrological cycle. Another source of heavy metals to groundwater are the agricultural practices, which can cause a surplus of heavy metals, due to the use of pesticides, fertilizers and sewage sludge.

Water pollution by heavy metals as a result of human activities is causing serious ecological problems in many parts of the world. This situation is aggravated by the lack of natural elimination processes for metals. As a result, metals shift from on compartment within the aquatic environment to another, including the biota, often with detrimental effects. Where sufficient accumulation of the metals in biota occurs through food chain transfer, there is also an increasing toxicological risk for humans (Edmunds & Shand, 2008).

The variety of metal species is the main methodological difficulty in designing metal-based monitoring programmes. When checking compliance with water quality guidelines, for example, metals should always be determined in the same forms as those for which the guidelines or standards are set. If the quality standards refer to the dissolved forms of metals only dissolved forms should be monitored (Edmunds &

Shand, 2008).

5.4 Groundwater monitoring points

Locating the appropriate monitoring point locations is essential in designing a monitoring network capable of providing data of adequate quality to achieve the program objectives. However, deciding about the placement and construction of monitoring wells are among the most difficult tasks in developing an effective monitoring program. The preliminary locations and depths of monitoring wells should be selected on the basis of the best available pre-drilling data. Then as the actual installation of these wells progresses, new geologic and hydrologic data should be incorporated into the overall monitoring plan to ensure that the finished wells will perform the tasks for which they are designed. In most instances, it is probably advisable to select a minimum array of monitoring wells for the collection of geologic and hydrologic data. Then additional wells can be designed and constructed to meet the goals of the monitoring program more effectively (Barcelona *et al.*, 1985). If wells or boreholes already exist on the field they can be included on the monitoring network and therefore reducing costs. However, it is important that they have good supporting geological information and construction details. Short-screen lengths or partial penetrating in the aquifer are preferable. Still, it must be taken into account that short screened boreholes may have a small yield making sampling difficult when permeability is low. The use of large diameter and/or long screened wells for monitoring purposes should be avoided, and mild steel cased boreholes should be used with caution. In addition, the use of existing water supply wells for monitoring purposes may lead to the collection of water samples that may be a mixture of water from different aquifer layers, and sampling quality may be variable with time and pumping rates (Edmunds & Shand, 2008).

The density of monitoring wells should depend on the size and heterogeneity of the groundwater body, the geological and hydrogeological characteristics of the groundwater system, the aquifer vulnerability and the risk posed to the aquifer from potential contaminant sources. As each and every aquifer is unique, ideally the selection of sites should be based on local knowledge and experience, and sampling point density may change according to local conditions. Within the available budget, sampling sites should not only be representative but also be able to monitor geochemical evolution along the same flow path. Given the long turn over time of most aquifers, water quality distribution is the result of former flow patterns and may not follow current ones, especially when aquifer development is intense. Then, flow paths to be considered depend on the new circumstances and the pumping regime (Edmunds & Shand, 2008).

The positioning of a monitoring point in a contaminant flow path must be based on hydrologic data. Therefore, the contaminant flow path must be clearly defined in three dimensions. The flow path can be attained, for instance, using a conceptual model representing the study area. Additionally, geostatistical analysis can also be used to optimize monitoring well layout, either prior to implementing the groundwater monitoring program or during periodic reassessments of the monitoring programme.

As well drilling and construction progress, special emphasis must be placed on the collection of accurate groundwater level data. Accurate measurements of stabilized water levels from an established reference elevation are essential to understand the groundwater flow path (Barcelona *et al.*, 1985). In addition, the knowledge of the vertical distribution of groundwater quality is extremely important as it provides a three-dimensional understanding of the flow system.

The construction of the borehole itself is very likely to disturb the local groundwater flow regime, especially for boreholes situated in recharge or discharge areas, giving rise to significant vertical components of groundwater flow. A borehole may also go through two or more aquifers separated by impermeable strata. Different hydraulic heads may produce upward and downward components of flow and the borehole itself may induce cross-contamination by permitting flow from one aquifer to the other. Vertical sampling of the aquifer under unconfined conditions may identify a gradation in water quality, with modern, often polluted waters overlaying older pristine groundwater. Understanding this stratification through logging and monitoring is important for the overall protection of the groundwater resource (Edmunds & Shand, 2008).

The type of drilling equipment selected should depend on the type of geology present, the expected depths of the wells, and the need to minimize the disturbance of the subsurface geochemical conditions. However, the availability and relative costs of different types of drilling equipment should not be used as the primary selection criteria. The use of specialized drilling techniques may have real advantages for even the most preliminary site investigations (Barcelona *et al.*, 1985).

The next figures illustrate examples of localization of the monitoring points. As shown, the potential sources of contamination and the aquifers in study should be characterized previously to the development of a groundwater monitoring network, since the selection of target monitoring zones cannot be made until the both source and aquifer have been evaluated. Usually, this assessment can be performed by a detailed hydrogeological evaluation of the site. Again, the importance of the knowledge of preferential path flow (preferably in 3D) is underlined, as a two-dimensional analysis may not reveal the actual up gradient or down gradient locations of groundwater flow. The presence of vertical gradients may significantly affect the selection of monitoring locations (Delleur, 2007).

It is also important consider the expected pollutants to be present in the definition of sampling points for groundwater collection, once the collection must be adapted to the type and configuration of the pollution plume and its hydrogeochemical properties. Pollutants have different behaviours, and depending on their solubility and density they may be found on either the top or basis of the aquifer. Having this, proper sampling will avoid situations where some elements are not detected because of an inappropriate conception of the distribution of the pollution plume (Leitão *et al.*, 2008).

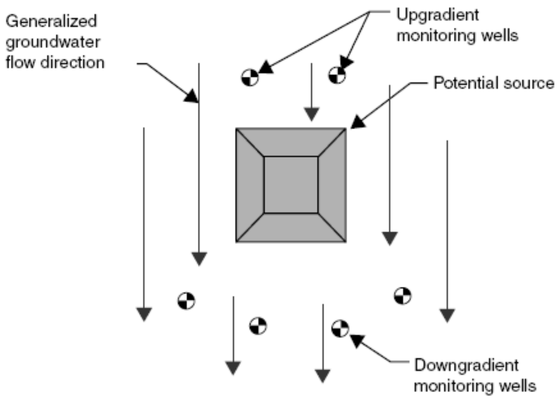


Figure 6 – Plan view of typical unconfined aquifer groundwater monitoring system. Source: Delleur (2007).

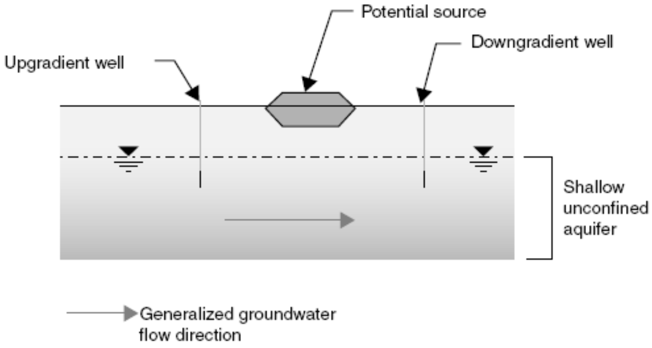


Figure 7 – Section of typical unconfined aquifer groundwater monitoring system. Source: Delleur (2007).

As shown in the figure below, the locations and orientation of confining units have a significant effect on potential contaminant migration paths, and therefore in the vertical spacing of monitoring wells.

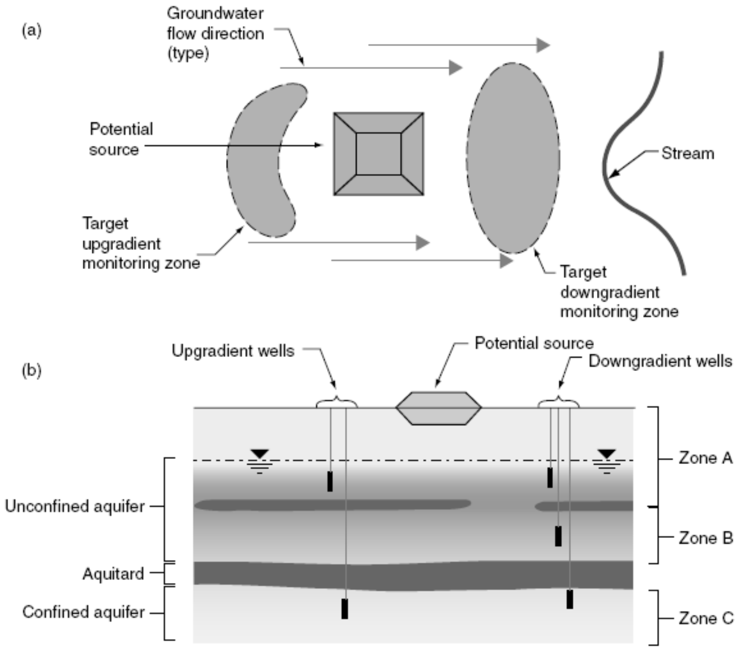


Figure 8 – (a) Horizontal target monitoring zones; (b) Vertical target monitoring zones. Source: Delleur (2007).

5.5 Sampling frequency

Groundwater sampling is quite different from surface water sampling, mainly due to the different hydrodynamic characteristics of both media, even though there are some other different aspects regarding these two types of water bodies. Indeed, when for surface water it is possible to collect samples in different points of a water stream, upstream and downstream of the pollutant discharge event, for groundwater it is not so easy to detect a direct cause-effect relationship. Runoff water infiltrates at very low velocities, making it hard to determine the time it takes to arrive to a borehole. Moreover, groundwater flow paths are not linear, due to dispersion processes (Leitão *et al.*, 2008).

Barcelona *et al.* (1985) suggest an approach beginning with a first evaluation of the type of source that is being monitored: a spill, slug, intermittent source, or continuous source. Then it should consider the likely pulse or continuous plumes of contaminants to be monitored, determine the minimum desired sampling frequency in terms of length along the groundwater flow path, and use hydrologic data to calculate the required frequency to satisfy these goals. However, ultimately, sampling frequency will result from a balance between the required number of samples to have representative data and the available budget.

In the initial monitoring phases, and whenever possible, it is recommended to realize more frequent measurements of the main parameters, like pH, electrical conductivity, temperature, dissolved oxygen and redox potential, using proper devices. When quality trends in water quality are identified along a given period, it is possible to adopt a sampling frequency that better adjusts to the representative sampling collection (Leitão *et al.*, 2008).

5.6 General guidelines of monitoring techniques and methods

Previous to sampling collection it is important to perform field measurements without disturbing the system with the sampling action itself. This process is called monitoring in static conditions. Generally, it should occur at least with one week of interval between the installation of a new well and the collection of any kind of information, allowing the reestablishment of the natural aquifer conditions (Leitão *et al.*, 2008).

Literature suggests the continuous measurement, with the aquifer in balance, of the parameters electrical conductivity, pH, temperature, and, if possible, dissolved oxygen, total dissolved solids and redox potential. To register these parameters it can be used a multiparameter probe, shown on figure 9. This device can be used at different depths. This type of measurements supply a first approach to the vertical change of water properties, particularly if there is any stratification on the water column. Measurements should be realized as the probe goes down to avoid any water mixture.

Figure 9 – Multiparameter probe

A general approach to the sampling of groundwater monitoring wells should include a set of steps, for each monitoring point, which are ahead described (Leitão *et al.*, 2008, Delleur, 2007).

- Localize and identify the groundwater monitoring point by using, for instance, a GPS device. Every point in the monitoring network should be identified with a unique code.
- Inspect wells and surrounding areas – the well should be examined for evidence of tampering, damage, or other activity that could compromise its ability to produce a representative groundwater sample. The surface area surrounding the well should be examined for signs of recent activity, and

attention should be paid to eventual changes since the last sampling event. In case changes occur, it may be necessary to verify the adequacy of the monitoring well network layout. Observations should be recorded for further reference.

- Measure depth to groundwater table and total depth of the well – there are many techniques available for measuring the depth to groundwater in a well, including hand measurement using a wetted tape (which is simple and inexpensive, but somewhat time consuming), and electronic measurement (which is more expensive, but less time consuming, and can be configured to provide a continuous record of data, if needed). All measurement equipment should be decontaminated before being introduced into the well. Measurements of the depth to groundwater that are made shortly after sampling the well may not be representative of the actual depth to groundwater. Measurement of the total depth of a well is important for evaluating changes in the total depth.

- Collect groundwater samples – groundwater in the well should be collected using proper sampling techniques, which will be ahead described. Extreme care should be taken when collecting, preserving, storing and shipping groundwater samples to provide samples to the laboratory that are representative of groundwater quality. Sample quality is much more likely to be compromised in the field than in the controlled environment of a laboratory. All samples should be correctly identified. In contaminated areas, sampling should begin the most contaminated well, if any sampling equipment is to be used at more than one well. This will reduce potential cross-contamination between samples and minimize decontamination efforts.

- Measure physical-chemical parameters of the collected samples – parameters like pH, redox potential, electrical conductivity and temperature should be measured in situ and correctly recorded. The sample used to measure these parameters should be rejected. The electrodes should be washed previous to the measurement with water proceeding from the sampling point. After the measurement, the electrodes should be washed with distilled water and correctly stored.

- Document sampling event – during the sample event, each step of the sampling process should be documented to allow detailed examination of the sampling procedures in the future. Good documentation is essential because it provides the bases for verifying the validity of the monitoring event. The sampler should also indicate in particular any problems that arose. The recording of the samples must to be done by attaching an appropriately inscribed tag or label. A record of every sample collected has to be completed, offering positive sample identification and sufficient information including:

  - name of the sample collector;
  - date;
  - time;
  - exact location, a detailed description of the sampling points (by maps, direction, GPS coordinates or landmarks);
  - water temperature;
  - any other data that may be needed for correlation, like for instance weather conditions, or post sampling handling.

When the sample is transferred, the label on the bottle should contain both the name of the person assuming sample custody and the time and date of transfer.

The monitoring plan should include a written protocol of the sampling procedures, including instructions and tasks to perform, considering the following aspects (Leitão *et al.*, 2008):

Material preparation in the laboratory:

- Verification of the equipment to measure in situ parameters, including calibration of the electrodes;
- Verification of the equipment to measure groundwater level and of the GPS device to locate the monitoring point;
- Verification of all the collection material (bottles, automatic or manual sampler device);
- Bottle separation according to the parameters that will be analyzed;
- Correct and clear bottle identification;
- Preparation of diverse supporting material (e.g. pipette, pH tapes, filtration system);
- Preparation of conservative solutions, if needed;

- Personnel protection materials (e.g. gloves, boots);
- Thermic boxes;
- Cleaning material (e.g. distilled water, water and paper);
- Documents (e.g. notebook, pen, tags).

General aspects to consider during sample campaign:

- Verify weather conditions and adopt measures to conserve samples during sampling campaign, once some chemicals can degrade faster under high temperatures;
- Secure that samples are not infected by inadequate handling (absence of gloves or washing of equipment used during the collection) or during transportation and storage (temperature change, unsuited container type, inadequate conservation time, etc.);
- Collect enough volume of sample to realize the required determinations, as well as repetitions and quality tests;
- Fill up the bottles completely, in order to guarantee that there is no air in the surface of the water sample when the cover is placed. Still, the bottle should not be totally filled in order to:
  - Avoid pouring out in case of analysis of elements with a different density from water;
  - Allow the liquid to expand due to changes in volume when the sample needs to be frozen;
  - Shake the sample bottle due to the presence of suspended material.
- When collecting a sample in a groundwater monitoring point with a pump using a tap the water should run for at least 5 to 10 minutes before being collected.
- Measure both depth to water table and the geometrical characteristics of the monitoring point: diameter, depth and casing height above ground surface.

Procedures to collect samples:

- Make a record of every collected sample and identify every bottle with a unique sample number, preferably by attaching an appropriately inscribed tag or label;
- Wash sampling devices with distilled water;
- Measure temperature, pH, electrical conductivity, redox potential, dissolved oxygen placing the electrodes submerged and about 2 cm away from the side and bottom of the water container; wait some minutes and register the parameter’s value;
- Wash the bottles at least twice with sampling water, unless they contain conservative substances or are sterilized;
- Collect the water sample directly on the bottle that will be transported;
- Use proper bottles according to the parameters that will be analyzed;
- Fill in a field report with sample identification, date and place of collection and parameters that will be analyzed.

A sample has to meet the requirements of the sampling program and to be handled in such a way that it will be not deteriorate or become contaminated before it reaches the laboratory. Some general precautions to be taken include:

- For samples that will be shipped, it is recommended to leave an air space of about 1% of container capacity to allow for thermal expansion;
- For samples containing organic compounds and trace metals special precautions are necessary, because of small concentrations (mg/l) of some constituents, they may be totally or partially lost if proper sampling and preservation procedures are not followed.

5.7 Groundwater sampling methodologies

A Sampling Procedure can be defined as the succession of steps set out in a specification that ensures that the sample eventually taken for analysis will possess the essential characteristics of the bulk (population).

Groundwater sampling typically requires extracting and collecting a volume of groundwater from a monitoring device for subsequent analysis. The two most common types of samples are grab samples or composite samples and can be obtained either manually or using an automated sampler.

Grab samples are single samples collected at a specific local over a short period of time. Thus, they represent a snapshot in both space and time of a sampling area. Discrete grab samples are taken at a selected location, depth and time, meaning that the sample can only represent the composition of its source at the time and place of the collection.

However, when a source is known to be relatively constant in composition over an extended period of time or substantial distances in all directions, the sample may represent a longer time period and/or a larger volume than the specific time and place at which it was collected. In these cases, a source may be adequately represented by single grab samples. Examples include protected groundwater supplies, but rarely groundwater plumes.

When a source is known to vary with time, grab samples collected at suitable intervals and analyzed separately can document the extent, frequency and duration of these variations. Sampling intervals should be defined based on the expected frequency of changes that may have, for instance, a seasonal period. When the source composition differs in space samples should be collected from appropriate locations in order to meet the goals of the study. Examples here include sampling upstream and downstream of a pollution point source.

Composite samples should provide a more representative sampling of the heterogeneous matrices in which in the concentration of the analytes to be analyzed may vary over short periods of time and/or space. This kind of samples can be obtained either by combining portions of multiple grab samples or using specially designed automatic sampling devices. Time sequential composite samples are collected by using continuous, constant sample pumping or by mixing equal water volumes collected at regular time intervals.

The advantages of this type of sampling include reduced costs of analyzing a large number of samples, more representative samples of heterogeneous matrices and larger sample sizes when amounts of test samples are limited. The disadvantages of composite samples include loss of analyte relationships in individual samples, potential dilution of analytes below detection levels, increased potential analytical interferences and increased possibility of analyte interactions.

However, time composite samples should be used only for determining components that can be demonstrated to remain unchanged under the conditions of sample collection, preservation and storage. Such determinations should be made on individual samples as soon as possible after collection and preferably at the sampling point. Analyses for all dissolved gases, residual chlorine, soluble sulphide, temperature, and pH are examples of this type of determination. Changes in such components as dissolved oxygen or carbon dioxide, pH, or temperature may produce secondary changes in certain inorganic constituents such as iron, manganese, alkalinity, or hardness. A procedure to collect this type of samples consists in collecting individual portions into a bottle every fixed period of time and mix at the end of the sampling period. If preservatives are used, they should be added to the sample bottle initially so that all portions of the composite are preserved as soon as collected.

Automatic sampling devices are also available. Still, when composite samplers are running for extended periods (weeks to months) should undergo routine cleaning of containers and sample lines to minimize sample growth and deposits.

Integrated samples are another type of sampling procedures. For certain purposes, the information needed is provided best by analyzing mixtures of grab samples collected from different points simultaneously, or as nearly so as possible. Such mixtures are called integrated samples.

Groundwater sampling methods can be one of the following (Standard Methods for the Examination of Water and Wastewater, 1998):

- Manual sampling – this type of sampling involves minimal equipment but may be excessively costly and time consuming for routine or large scale sampling programs. It requires train field technicians and is often necessary for regulatory and research investigations for which critical assessment of field conditions and complex sample collection techniques are essential.

- Automatic sampling – automatic samplers can eliminate human errors in manual sampling, reduce labour costs and provide the means for more frequent sampling.

The groundwater sampling techniques most often used to collect samples from monitoring wells include the low-stress approach (or low-flow sampling, minimal drawdown sampling), the well volume approach, the minimal purge approach, discrete interval sampling and passive sampling (Delleur, 2007). Selecting the appropriate sampling technique is based on several factors including well construction, hydrogeologic characteristics of the site and the proposed analytical requirements. Groundwater sampling methods vary based on the type of device used, the position of the sampler intake, the purge criteria used and the composition of groundwater to be sampled (e.g. turbid, containing high volatile organics). All sampling methods should be clearly documented. Table 4 includes a set of guidelines of monitoring well purging and sampling approaches.

Table 4 - Applicability of different approaches for purging and sampling monitoring wells. Source: Delleur (2007)

	Low stress approach	Well – plume approach	Others (Such as passive diffusion samplers, in situ samplers, and other non-traditional groundwater sampling pumps)
Applicable Geologic Materials	Materials with moderate to high hydraulic conductivities. May be applicable to some low hydraulic conductivities, if can meet minimal drawdown criteria.	Material with low to high hydraulic conductivities.	Materials with very low to high hydraulic conductivities.
Aquifer/Plume Characterization Data Needs prior to Choosing Sampling Method	High definition of vertical hydraulic conductivity distribution and vertical containment distribution.	Plume and hydraulic conductivity distributions are less critical.	May need to consider the degree of hydraulic and contaminant vertical distribution definition dependent on Data Quality Objective sand sampler type.
Constituent Types Method is Applicable	Mainly recommended for constituents that can be biased by turbidity in wells. Applicable for most other contaminants.	Applicable for all sampling parameters. However, if turbidity values are elevated, low-stress approach may be more applicable if constituents of concern are turbidity sensitive.	Constituents of concern will be dependent on the type of sampler.
Data Quality Objectives	1) High resolution of plume definition both vertically and horizontally. 2) Reduce bias from other sampling methods if turbidity is of concern. 3) Target narrow sections of aquifer.	1) Basic characterization 2) Moderate to high resolution of plume definition (will be dependent on screen length). 3) Target sample composition to represent entire screened/open interval.	1) Can be applicable to basic site characterization, depending on sampler and methodology used. 2) Can reduce bias from other sampling methods. 3) May yield high resolution of plume definition.

The low stress approach is based on the assumption that purging and sampling at a low flow rate that minimizes the drawdown in the well allows sample to be obtained from the aquifer formation at a discrete interval with minimal interaction with stagnant water in the well column. This approach is performed using a variable speed sampling pump to extract water from the screen interval at a low flow rate, typically between 0,1 and 0,5 l/min. During well purging, drawdown within the well is monitored and the flow rate adjusted to minimize drawdown to less than 0,1m from the static water level in the well.

In order to minimize potential effects of the quality of the obtained sample, the well should be purged at a flow rate that does not produce turbulence within the well. Minimizing turbulent flow will reduce the potential for volatilization or excessive turbidity. Care should also be taken to minimize the drawdown below the top of the screened interval of the monitoring well that could expose the aquifer to the atmosphere. When the minimum number of well volumes is purged, samples can be collected into proper containers filled directly from the pump discharge and prepared for analysis. During well purging, the discharge is typically routed through a flow through cell and selected water quality parameters are monitored using portable field monitoring probes. Purging is continued until the values for these parameters stabilize. Following stabilization, samples can be collected directly from the discharge of the pump at the same flow rate that was used during well purging. This type of approach provides samples that are representative of the mobile load of contaminants present (dissolved and colloidal phases), minimizes sample disturbance and reduces the volume of purge water that oftentimes is subject to special treatment or disposal requirements. The disadvantages of this approach include additional capital costs for specialized equipment, additional personnel training requirement and greater set up times in the field (Delleur, 2007).

The well volume approach is another sampling approach commonly used. In this case, the volume of the standing water column in the monitoring well is calculated based on water level measurements and well construction details. The well is then purged until a minimum number of well volumes, typically between three and five volumes have been extracted. The pump is placed in the water column to a depth that will not result in drawdown below the pump intake that could allow air to enter the pump. In addition, the pump should be lowered slowly and set sufficiently above the bottom of the well to minimize disturbance by the presence of sediments that could affect sample integrity. This approach can be performed using either dedicated or portable pumping systems. The advantages of this type of approach are the easiness of implementation, cost, availability of sampling equipment, comparability with historical results and minimal training requirements for field personnel. The disadvantages are related to sample representativeness, which may be sometimes compromised due to increased stress of the formation that may allow preferential flow from areas outside of the discrete zone. Moreover, increased flow rates create turbulence in the well that can result in loss of volatile compounds, oxidation of samples and entrainment of sediments into the sample (Delleur, 2007). All the previous cited can affect data quality.

The minimal purge approach is generally used in low yielding zones, when purging prior to sample collection is not possible. This approach is typically performed with dedicated, downhole sampling equipment to set a discrete depth within the screened interval. Purging is performed in a way that only the water volume contained within the sampling system is evacuated with no attempt to remove water from the well casing or formation. Sample is collected directly from the discharge of the sampling equipment. Attempts should be made in order to minimize the purge volume by using small diameter tubing and the smallest sampling chamber possible (Delleur, 2007).

Passive sampling techniques include sampling protocols that are used to collect a sample of environmental media for analysis, but sample is not an aliquot of groundwater. Passive samplers also rely on formation water moving through the well screen or open interval, rather than forcing water through the well by evacuating groundwater from the well screen or applying a vacuum. This type of sampling typically makes use of specialized sampling media that interact with the groundwater in the well. The contaminants in the well are then transferred to the media via physical processes such as diffusion or sorption and the sampling media is extracted and analyzed (Delleur, 2007).

5.8 Groundwater representative sampling

Sampling collection is a very important step of the monitoring plan. The sample eventually analysed will in most cases, be a very small part of the material to which the analytical result relates. Yet it is on the basis of this result that a commodity is, for example, purchased, sold or dispensed.

Sampling can involve very complex procedures, often including many stages of sub-division before the analytical result is finally obtained. If, at any of these stages the sample taken is not representative of the bulk of the material from which it was taken, then the result reported will be inaccurate. In modern terminology the general term "sample" has been replaced by the more precise term "representative sample".

A representative sample can be defined as a portion of a material taken from a consignment and selected in such a way that it possesses the essential characteristics of the bulk.

In fact, we should experience few sampling problems if all materials to be sampled were known to be homogenous. Gases and liquids are often considered to be homogeneous though this is not always so.

Thus some form of mixing must be considered before a strictly representative sample can be taken.

Sampling therefore can be a very complex procedure. In addition, we have no way of knowing that the portion of the material eventually analysed does truly represent the bulk of material from which it was taken. Therefore, we rely to a large extent on a statistical approach to sampling, a reliable sampling procedure being developed for a particular situation only after considerable experimental work has been carried out. Even then the method actually chosen to take the sample is the one that appears to give the correct answer. The true answer, of course, is available only if all the material (population) is analysed or tested, obviously an impossible situation. Statistics therefore plays an important part in the design of any sampling procedure.

When we attempt to develop an effective sampling procedure some important factors must be considered, such as:

- the sample taken must be representative of the bulk (population),
- the quantity of sample to be taken must be determined,
- the handling and subsequent storage of the sample must be correct.

5.9 Equipment

There is little point in taking great care in extracting a sample, if it is to become contaminated, or a portion of it lost before the analysis is carried out. Therefore, for this reason, sampling instruments and containers should be clean, and made of a material that is inert to the substance to be sampled. In addition, to eliminate the possibility of changes occurring in the sample, there should be a plan to analyse the sample as soon as possible after it has been taken.

The choice of the right 'type of person' to carry out the sampling is not easy. The sampler must be conscientious, and capable of following precisely any given set of instructions. Above all, the sampler must be aware of the importance attached to the sampling procedure, and be capable of taking decisions when the unexpected occurs.

Automatic samplers are becoming increasingly popular, but they may be subject to bias unless they are rigorously tested before introduction and carefully maintained a calibrated regularly.

Monitoring equipment may consist of a commercially manufactured units or systems or may be constructed by the user or others from standard analytical systems. The commercial systems offer flexibility as to the parameters measured and often incorporate standardisation, cleaning and automatic testing systems. If the user has difficult requirements for analysis then such units may not need these demands.

To be able to show how certain activities affect the quality of the groundwater, it is important to take reliable and frequent measurements. Typically groundwater samples are collected in monitoring wells. However, piezometers and groundwater discharges are also used to collect samples. Each feature has a purpose and a situation for which it is best suited. Table 5 presents these features as well as some advantages and disadvantages of each one.

Table 5 – Groundwater monitoring features. Source: (Delleur, 2007).

	Primary use	Advantages and limitations
Wells	Groundwater sampling	Extensive record of successful use: Can be targeted to specific site limitations and contaminants of concern; Flexible design.
Piezometers	Groundwater potentiometric surface measurement	Allows measurement of potentiometric surface at a point; Can be outfitted to provide continuous monitoring of groundwater elevation; Not well suited for groundwater sampling.
Lysimeters	Sampling liquid from vadose zone	Allows characterization of liquid that could eventually impact groundwater quality; May allow loss of volatile organic compounds in samples; Construction materials may affect chemical composition of samples.
Seeps	Surface sampling of groundwater seepage	Low cost for establishing sampling point; Gives good indication of quality of water with which humans or organisms may come into contact.
Geophysical techniques	Plume delineation	Large areas can be quickly delineated at the survey level, inexpensively; Can be used on ground surface or in boreholes; Cannot be used to detect presence of specific constituents.
Sampling probes	Plume delineation	Allows quick sample collection without incurring the cost of installing a monitoring well: limited to one time sampling of groundwater.

The purpose of a groundwater monitoring well is to provide access to the target monitoring zone for collection of a representative sample of groundwater. The representativeness of the sample may be affected by both well installation or materials used on its construction. Even though a number of agencies and organizations, including the United States Environmental Protection Agency and the American Society for Testing Materials present standard approaches for designating groundwater monitoring wells, site specific conditions and applicable local requirements should be considered when designing a groundwater monitoring well.

Some key features of a groundwater monitoring well include the well screen, filter pack, bentonite seal, cement grout backfill, concrete apron and protective cover. The most important aspect of monitoring well design is the proper sizing and placement of the well screen or open interval.

When sizing the well screen both the screen interval size and screen length for the proposed monitoring well should be considered. The screen interval for the monitoring well should be sized based on the geologic materials outside of the screened interval and the proposed filter materials and should be limited to the target monitoring zone. The screen length should be minimized to avoid dilution in the screened zone and to reduce potential contaminant migration to other zones within the aquifer. The filter pack is intended to promote formation of a graded filter outside of the well to prevent migration of fine grained soils into the well and should also have a characteristic particle size (i.e. the diameter greater than 85%, by weight, of the soil particles) bigger that the well screen slot size to prevent clogging of the well screen by the filter pack material. Similarly, the filter pack material should be capable of retaining the remaining 15% of materials in the geological formation. The bentonite seal is intended to prevent the cement grout backfill from migrating into the filter pack, as the presence of grout in the filter pack could permanently compromise the validity of groundwater samples from the well. The concrete apron is intended to route surface water away from the well and to prevent downward migration of surface water into the well screen (Delleur, 2007). The protective cover aims to protect the pipe inside the well, as well as the well itself from any kind of unauthorized access.

Figure 10 presents typical groundwater monitoring well designs, but both of them can be modified to meet specific site conditions. The design shown in figure 10 (a) incorporates several features that minimize the possibility of introducing contaminants into the well (e.g. the protective cover, the bentonite seal and the well apron). The monitoring well presented in Figure 10 (b) is typically used where the well must be installed beneath a confine feature, where the additional casing prevents leakage from the upper to the lower aquifer or through a heavily contaminated soil layer, where the additional casing prevents mixing of drill cuttings from the target monitoring zone with the contaminants in the overlaying or underlying portion of the aquifer (Delleur, 2007)

When installing a groundwater monitoring well some questions should be considered, in order to avoid potential problems. The construction materials used on the well should not be physically or chemically incompatible with neither the surrounding natural earth materials nor contaminants in the area being monitored. These materials should also be strong enough to prevent collapse due to the stress applied by the soil.

When it comes to select a proper a well screen size, it should be considered that too large screen sizes might allow siltation of the well. On the other hand, too small screen sizes may prevent proper development of a graded filter around the well. The screened interval of the well should be correctly placed across the stratigraphic zones, if the aim of monitoring is to sample discrete zones of the aquifer. The filter pack material should be correctly selected and placed, in order to avoid either siltation of the well or plugging of the well screen. Again, an improper selection or placement of annular seal materials can allow plugging of the filter pack, cross-linking of discrete water bearing units or migration of grout into the filter pack.

Regarding surface protection measures of the well, it is important that they guarantee that no damage is caused to well casing materials and no surface water enters into the well at ground surface. Evacuation techniques should also be adequate in order to avoid changes in the aquifer formation around the well screen, which may cause excessive siltation of the filter pack and groundwater samples, or compromise well yield.

Piezometers are used to measure the hydraulic head at a specific location within the aquifer and are not designed for the collection of groundwater samples. Typical attributes of a piezometer include a small diameter borehole, casing, a screen to minimize the impact of the piezometer on groundwater flow in the aquifer, a small screened interval (because long screened intervals provide the average head over a large depth instead of the head at a specific location), small or no filter pack as it may impact the hydraulic head near the screened interval of the piezometer, and a very effective seal at the top of the screened interval, in order to prevent intrusion of water from above the measuring point (Delleur, 2007).

The control of a single monitoring point whether by timer, programmable logic controller, or computer, is relatively simple. Where several instruments are used to monitor a sample source the control and data acquisition functions require more careful consideration. If each device was controlled separately then the data obtained may not be coordinated. Further actions, such as cleaning and calibration may have a deleterious effect on other sensors which are not simultaneously being cleaned or calibrated, but are also not disabled.

The preferred option is to place the complete monitoring system under one master controller. This has then the function of coordinating all the actions within the station and can supervise data gathering and telemetry (if something more sophisticated than chart recorders are required). The controller should be chosen carefully and consideration given to the following points:

- Does it relate to a real time clock (e.g. exact time and data)?
- Does it have enough channels of the correct type of input and output to control all the instruments to be connected, and does it have the correct input channels to monitor all the data and status inputs in the station?
- Can it recover from a power failure and maintain integrity of data?
- Can it take intelligent decisions regarding the data and status inputs?
- Can it communicate easily with other communication and data systems within the organization?
- Apart from reports is data available in a flexible transportable form so that it may be used in other data processing systems by other personnel?

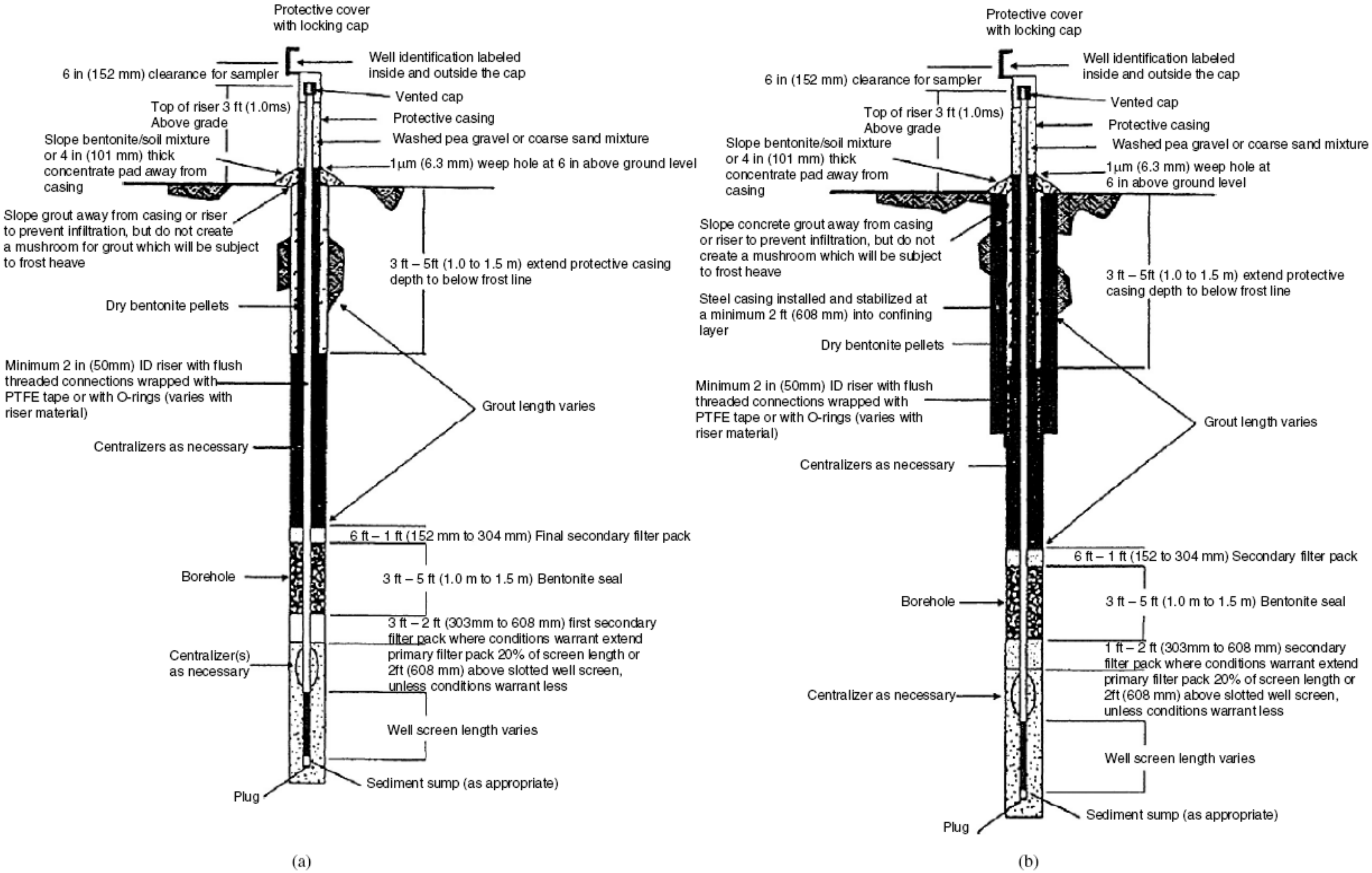


Figure 10 – Monitoring well design. Source (Delleur, 2007).

Locations like springs, seeps, drains or other groundwater discharges such as production extraction wells can also be used to collect groundwater samples. Typically, they provide a measure of groundwater quality at a location where a receptor may be present (for instance a drinking well or discharge to a surface water body) and for this reason this type of locations are often incorporated into groundwater programs and used as a point of compliance. However, there should be some previous verification of the monitoring programme to check if the groundwater quality obtained in these discharge locations is comparable to the data collected at other monitoring points in the programme. Other situation to account for is the variability in groundwater quality at discharge locations, due to the interaction with the atmosphere and dilution with surface water bodies or groundwater from outside the study area. This variability can affect contaminant concentrations observed in discharge samples and prejudice the results of the analysis. Groundwater monitoring programs may also incorporate alternative monitoring devices that may provide:

- Short term data to supplement the conventional monitoring program or indirect data that can be inferred to assess potential releases (i.e. geophysical variations);
- Data regarding conditions outside of the target monitoring zone (e.g. vadose zone) that can be extrapolated to assess groundwater quality within the monitoring zone.

Often these techniques are incorporated into monitoring programs at sites that may be small, dry or remote, where the use of conventional groundwater monitoring devices sampling techniques may be impractical or cost prohibitive (Delleur, 2007).

Various surface and borehole geophysical methods including for instance electrical induction or electromagnetic induction and induced polarization can be used to monitor variations in aquifer and groundwater properties that can be indicative of releases. Geophysical evaluations are quite useful in plume delineation and their monitoring can provide a general measure of changes in the aquifer system, bus most are not sensitive enough to detect minor changes in concentrations or provide precise concentration values for specific contaminants that may be of interest. Soil gas probes and soil gas survey data can be used to infer impacts on groundwater quality from some volatile compounds in shallow groundwater regimes. Soil gas surveys involve inserting a temporary or permanent probe or tube into the vadose zone and extracting gas from the subsurface to collect a sample. The soil gas data do not provide a direct measurement of groundwater quality and are limited to assessing volatile compounds. Moreover, soil gas samples require special handling and shipping considerations (Delleur, 2007).

Lysimeters are a method used to study percolation and leaching losses of soil by collecting water samples from the vadose zone, either passively (by gravity collection) or through applying a vacuum or pressure to extract water from the unsaturated soils. The first type is called plate lysimeter and collects soil water as it percolates down via gravity through saturated soils. The second type, called suction lysimeters, is installed below ground level and vacuum is applied to the device through a tube leading from the lysimeter to the ground surface. The negative air pressure created inside the lysimeter draws pore water into the lysimeter through the porous, stainless steel section of the lysimeter. The pore water is transported to the surface by applying positive pressure to the lysimeter through a second tube. At the surface the pore water is collected in a collection bottle. However, lysimeter samples are sometimes difficult to obtain and pressure changes induced by some devices may affect the solution chemistry of some contaminants and, in consequence, affect data quality. Typically the use of this type of devices in a groundwater monitoring programme occurs in recharge areas. Data acquired here can be used to obtain concentration data for waters recharging the aquifer through the zone that may be used to evaluate contaminant flux and fate transport.

Some groundwater monitoring programmes may include the use of direct monitoring devices, such as downhole sensors or probes that can analyze groundwater quality in situ. Multiparameter probes can be used for both in situ and in different depths measurements of the physical characteristics of water. These probes (Figure 11 shows an example) can be equipped with different electrodes, allowing monitoring several parameters simultaneously: pH, redox potential, electrical conductivity, temperature and dissolved oxygen. To guarantee the quality of the measurements, the electrodes should be calibrated with adequate standard solutions. These solutions are generally provided with the equipment, and each parameter as its proper type of solution.

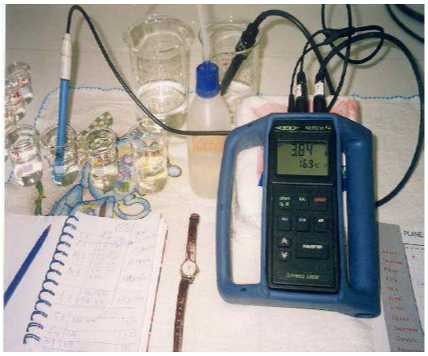


Figure 11 – Probe with electrodes

Ion selective probes are another type of direct device commonly used at groundwater monitoring sites. These devices are designed to detect specific ions in groundwater, by producing an electric signal that can be compared to a reference signal for a specific ion constituent. This method is particularly useful for preliminary both groundwater characterization and tracer studies.

Optic fiber chemical sensors are intended to detect a specific chemical in groundwater. The sensor is made of a reagent that is physically confined or chemically immobilized at the end of a fiber optic cable. The cable is inserted into the monitoring well, piezometer or borehole and a signal is transmitted through the cable, which detects the constituent, if it is present. This method can be used on an extremely variety of constituents, uses portable equipment and produces results at a very low cost (Delleur, 2007).

Sampling devices are the most important equipment used to collect water samples. They are used to collect on point samples, which means they only represent water characteristics on the moment water is collected.

Figure 12 - Sampling devices used to collect groundwater samples

The procedure used to collect groundwater samples with this equipment consists on placing the device inside the monitoring point, at a given depth. It is necessary to wait some minutes before collecting the sample, in order to restore water’s natural circulation processes.

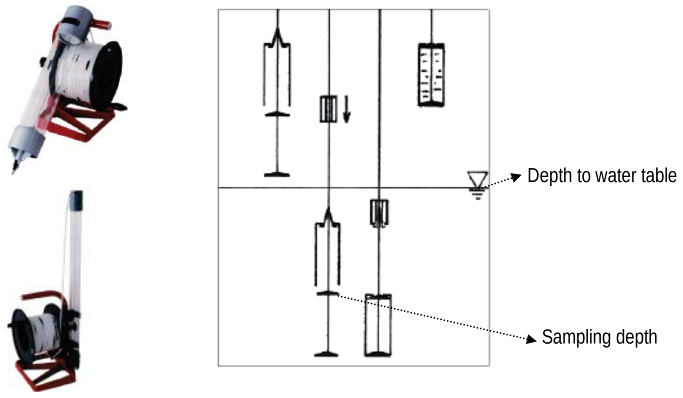


Figure 13 - Groundwater sampling devices and schematic representation of its operation. Source: Leitão *et al.*, (2008)

The diver allows automatic measurement and registration of groundwater levels and groundwater temperatures. This equipment can be installed on the monitoring well, suspended from a steel wire. Once installed, no part of the monitoring system is left above the ground level, which reduces the risk of vandalism. The diver measures automatically both groundwater level and temperature and registers these data in the internal memory, in a 10 minute time interval and cover a 6 month period. This device needs to be programmed with location, starting time, rate and measuring frequency. Data from diver can be collected with a laptop.

In certain circumstances, sampling can be an extremely hazardous operation. Safety harnesses and suitable protective clothing should be used when necessary, and often it is advisable that samplers should work in pairs for added protection.

Figure 14 - Diver operation. Source: http://www.surechem.com.my/

The sampler working alone and without adequate protection is likely to be less conscientious than is required for this important operation. Because sample constituents can be toxic, take adequate precautions during sampling and sample handling. Toxic substances can enter through the skin and, in the case of vapours, through the lungs. Inadvertent ingestion can occur via direct contact with foods or by absorption of vapours onto foods. Precautions may be limited to wearing gloves or may include coveralls, aprons, or other protective apparel. Eye protection should always be used. When toxic vapours might be present, sample should be performed only in well-ventilated areas or a respirator or self-contained breathing apparatus should be used. In a laboratory, sample containers should be opened in a fume hood. Never have food near samples or sampling locations.

If flammable organic compounds may be present, adequate precautions should be taken. Prohibit smoking near samples, sampling locations, and in the laboratory. Sparks, flames, and excessive heat sources should be taken away from samples and sampling locations. It should be avoided build-up of flammable vapours in a refrigerator storing samples because electrical arcing at contacts of the thermostat, the door activated light switch, or other electrical components may trigger a fire or explosions. If flammable compounds are suspected or known to be present and samples are to be refrigerated, only specially designed explosion-proof refrigerators should be used.

When in doubt as to the level of safety precautions needed, an appropriately trained industrial hygienist can be consulted. Samples with radioactive contaminants require other safety considerations.

5.10 Calibration

Most of the systems used for water quality monitoring will require calibration, which should probably be carried out at least one per day. Exceptions requiring less frequent calibration such as temperature measurement are rare. Even if the analytical parameter is known to be stable over long periods, as in the case of electrical conductivity, effects such as physical fouling of the electrode will create the need for regular recalibration.

Some determinants such as conductivity may only require one standard point calibration whereas other sensors may require one multipoint calibration. Sensors with complex calibration curves are best avoided if possible, as linear or logarithmic responses are simpler to calibrate.

Calibration process will almost certainly mean that the sensing system is not available for measurement whilst it is proceeding. If multipoint calibration is carried out this may then occupy a considerable period of time, so multiple calibration is best performed as several separate calibrations.

It is often common practice to calibrate at regular times each day. This may be inadvisable, and calibration and cleaning times varied to avoid regular pattern. If the monitor is inoperative at regular times then certain regular events relating to water quality may be missed, statistical data may be less valid and if such down-times known, this may lead to pollution discharges being timed to coincide with these events so as to escape detection.

5.11 Fouling and Cleaning

Fouling of monitoring systems will occur in virtually every case of water monitoring. It results in the coating of sensors with debris and organic growth causing the performance of the sensor to fall. On-set of fouling can often be detected by a variation by in the calibration signal. This may be used to “trigger” a cleaning cycle automatically.

The problem should be tackled by both prevention and cure. Preventive action will only reduce the frequency of cleaning. An exception may be if a cleaning or non-fouling agent(s) can be added to the sample continuously without affecting the sensor.

The following techniques can be used to reduce or prevent rapid fouling:

- A high sample flow through the monitor.
- Careful design eliminating flow deadspots (choice of construction materials may also help).

- Stopping the flow to the monitor after pumping will allow larger debris e.g. grit etc. to be removed.
- Reducing light levels are reduced to a minimum within the system to inhibit algal growth.
- Certain sensors may minimise effects fouling by their design, e.g. the sacrificial thallium dissolved oxygen sensor.

After fouling has occurred, the following techniques, often used in combination, have been found to be effective:

- Purging the system with air and water;
- The use of ultrasound for cleaning surfaces;
- The use of cleaning and sterilizing agents such as sodium hypochlorite, either in cleaning cycles or in the form of the continuous bleed;
- Mechanical action using brushes or squeegees.

5.12 Sample conservation and storage

After the well has been sampled, the water must be properly transferred to the sample container and preserved for the transport to the laboratory. During sampling, every effort must be made to minimize changes in chemistry of the sample, through a correct collection, preservation and correct storage.

Sample collection refers to the transfer of the sample from the sampling device to the sample container. The contents of the sampling device should be transferred in a controlled manner that minimizes sample agitation and aeration, which can cause gasification of samples, allow release of volatile organics or cause oxidation and precipitation of metals in the sample. Groundwater oxygen content trends to diminish with depth, which means that sample contact with air provokes a quick change on its chemical composition. In order to minimize this, it should be avoided an extended air contact of the sampled water. In samples that will be tested for volatile organic constituents there should be no air in the sample containers, as it would allow volatilization of compounds during shipment.

The purpose of sample preservation is to minimize any physical, chemical, and/or biological changes that may take place in a sample from the time of sample collection to the time of sample analysis (Zhang, 2007). Three approaches (i.e., refrigeration, use of proper sample container, and addition of preserving chemicals) are generally used to retard volatile loss and chemical reactions such as oxidation, biodegradation and sorption.

The proper selection of containers (material type and headspace) is critical to reduce losses through several physical processes, such as volatilization, adsorption, absorption and diffusion. Coloured (amber) bottles help preserve photosensitive chemicals such as PAHs. The addition of chemicals is essential to some parameters for their losses due to chemical reaction and bacterial degradation. Chemical addition or pH change can also be effective to reduce metal adsorption to glass container walls (Zhang, 2007). All the sampling materials should be cleaned and quality assured before using. Table 6 presents a resume of sample conservation processes for a set of common groundwater parameters.

Table 6 – Resume of sample conservation processes. Source: Leitão *et al.* (2008) and Standard Methods for the Examination of Water and Wastewater (1998).

Parameter	Type of container	Conservation	Maximum holding time
Solids	Plastic (polyethylene or equivalent) or glass	Refrigerate	7 days
Hardness		Add HNO_3 until pH<2	6 months
COD		Analyze as soon as possible or add H_2SO_4 until pH < 2; Refrigerate	7 days
BOD5		Refrigerate	6 hours
TOC	Glass	Analyze as soon as possible or add HCl until pH<2; Refrigerate	7 days
Metals (general)	Plastic (polyethylene or equivalent) or glass, rinsed with 1 + 1 HNO3;	Add HNO_3 until pH<2	6 months
Oil and Fats	Glass wide-mouth calibrated	Add H_2SO_4 until pH<2; Refrigerate	28 days
Total Hydrocarbons	Glass		
Nitrate	Plastic (polyethylene or equivalent) or glass	Analyze as soon as possible, Refrigerate	48 hours
Ammonia	Plastic (polyethylene or equivalent), teflon or glass	Add H2SO4 or HCl until pH<2 or Refrigerate	7 days
Total Phosphorus	Plastic (polyethylene or equivalent) or glass	Add H_2SO_4 or HCl until pH<2 or freeze without any additive	28 days

Sulphate	Plastic (polyethylene or equivalent) or glass	Refrigerate	28 days
Dissolved gases (O2, CH4, CO2)	Glass	Dark	35 hours
Iron Manganese Sodium Potassium Calcium Magnesium	Plastic (polyethylene or equivalent) or teflon	Add HNO_3 until pH<2	6 months
Phosphate Chloride, Fluor Silicate	Plastic (polyethylene or equivalent), Teflon or glass	Refrigerate	35 hours 7 days 7 days
Phenols	Teflon or glass	Add H3PO4 until pH<4 or Refrigerate	35 hours

Sample conservation refers to the actions taken to maintain sample quality during transportation. Samples should be cooled to a temperature of 4 °C (in insulated coolers) as soon as possible after they are collected and should be maintained at that temperature until they are received at the laboratory. The blue ice, a synthetic glycol package in plastic bags and frozen is less effective then wet ice (frozen water) and dry ice is not recommended, because it freezes samples and causes containers to break. When samples are kept frozen in the freezer, containers should be filled up only to 90%, to avoid container breakage. Samples should be shipped in containers that minimize agitation of the sample and should be accompanied by proper documentation.

Although, even with proper preservation, no sample can be stored for an extended period of time without significant degradation of the analyte. The maximum holding time is the period of time a sample can be stored after collection and prior to analysis (or pre-treatment) without significantly affecting the analytical results. Maximum holding time starts at the moment of sampling and ends with the beginning of the analytical procedure. Samples that exceed this period of time should be discarded, in order not to jeopardize data quality (Zhang, 2007).

Each single event should be documented so that the validity of the sample collection, preservation and storage techniques can be verified in the future. Each step of the sampling event should be recorded, including the time of sampling, weather conditions, time required to purge the well, volume of water purged, purge water characteristics, decontamination procedures, sample equipment calibration and procedures for the preservation of samples (Delleur, 2007). These records should be kept for future reference.

6 STATISTICS IN SAMPLING

Statistical sampling is based upon the principle that all the particles or portions of the material (population) should have an equal probability of being present in the taken sample. The parameter (e.g. the content of one constituent) that is determined during the analysis, is assumed also to have a normal distribution of the population. If it were possible to take an infinite number of samples from the population and to analyse for this parameter in each sample taken, then the frequency distribution of this parameter should obey the normal distribution law, which is illustrated in Figure 15.

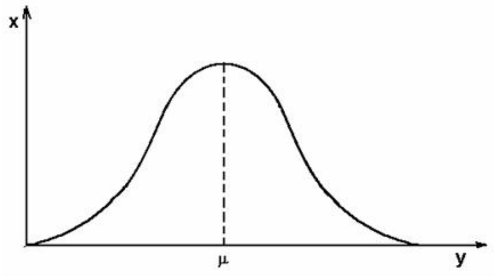


Figure 15 – Graphical representation of the normal distribution law

The equation of the normal distribution law is:

$$Y = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(x_i-\mu)^2}{2\sigma^2}\right] \qquad (2)$$

where

Y - variance of the population, σ - standard deviation of the population, μ - mean value of the parameter, xi - individual value of the parameter.

Variance is the square of the standard deviation, which is calculated by using equation 3,

$$\sigma = \left[\frac{\sum_{i=1}^{i=N}(x_i-\mu)^2}{N}\right]^{1/2} \qquad (3)$$

where N is the number in the total population, and when the true mean of the result is known, or by using equation 4 when μ is not known.

$$s=\left[\frac{\sum_{i=1}^{i=n}(x_i-\overline{x})^2}{n-1}\right]^{1/2} \qquad (4)$$

In this case μ is replaced by the estimated mean, $\overline{x}$, where $\overline{x}$ is the mean value of all the results obtained, σ is replaced by s where s is the sample standard deviation, and N by n, the number of results or observations. So, s gets closer to σ as the number of samples taken and analysed increases. However as the sample size decreases, the uncertainty introducing by using s to estimate σ increases. The extent of this uncertainty can be quantified by using equation 5.

$$\mu=\overline{x}\pm\frac{ts}{\sqrt{n}} \qquad (5)$$

where t is a statistical term obtained from the "Student's t-test table" (see table 7) and n is the number of results from which the mean is calculated. The value of ts/n1/2 is therefore the margin of error on either side of the calculated mean $\overline{x}$, within which we are confident that the true value lies. The extent to which we wish to be confident determines the value of t to be used.

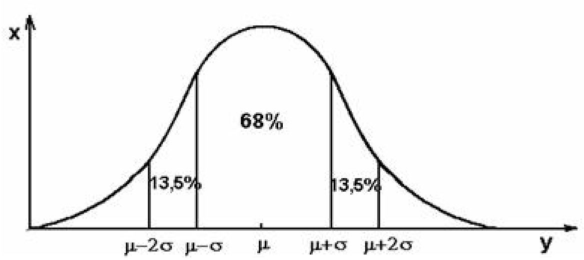


Figure 16 - Relationship of standard deviation to distribution

We can relate standard deviation to the distribution law given in equation 2, and show the relationship in graphical terms in the above figure.

From figure 16 we see that 68% of the analysis results obtained are within ± one standard deviation from the mean. About 95% are within ± two standard deviations.

In practice, of course, the individual constituents within the population generally do not have an equal probability of being present in the sample taken for analysis, because the sample will never contain only one completely uniform species. Hence there will always be an inherent variance (sampling error) in the composition of the sample eventually analysed. In addition to this, there will be the variance of the analytical result caused by the indeterminate (random) error in the analytical method adopted.

From equation 5, we see that the difference between the estimated mean value($\overline{x}$) and the true mean value (μ) is given by the term ts/n1/2.

Introducing the notation

$$E=t_s/n_{1/2}$$

and rearranging we obtain:

$$n=[t_s/E]2 \qquad (6)$$

where

s - prior estimate of the standard deviation of the 'lot' of material to be sampled, E - maximum allowable difference between the estimate to be made from the sample and the actual value, t - probability value chosen so as to give a selected level to confidence that the difference is not greater than E. This can be obtained from the 'Student's t-test table' (Table 7).

In using this equation we must assume that the value of the standard deviation of the component in the lot has been determined. This generally requires not less than thirty determinations being carried out on a single lot. If this is so the value of t is equal to 1.96 that can be approximated by 2.0.

Table 7 - Student's t-test table

Degrees of freedom	*Confidence level (%)*				
	80	90	95	99	99,9
1	3,08	6,31	12,7	63,7	637
2	1,89	2,92	4,30	9,92	31,6
3	1,64	2,35	3,18	5,84	12,9
4	1,53	2,13	2,78	4,60	8,60
5	1,48	2,02	2,57	4,03	6,86
6	1,44	1,94	2,45	3,71	5,96
7	1,42	1,90	2,36	3,50	5,40
8	1,40	1,86	2,31	3,36	5,04
9	1,38	1,83	2,26	3,25	4,78

10	1,37	1,81	2,23	3,17	4,59
11	1,36	1,80	2,20	3,11	4,44
12	1,36	1,78	2,18	3,06	4,32
13	1,35	1,77	2,16	3,01	4,22
14	1,34	1,76	2,14	2,98	4,14
>15	1,29	1,64	1,96	2,58	3,29

The overall variance is accepted to be the sum of the individual variances:

$$s^2=s_1^2+s_2^2 \qquad (7)$$

where

s1 - standard deviation of the sampling, s2 - standard deviation of the analytical measurement.

If one of the individual variances is more than ten times the other, the smaller of the two values will contribute very little to the overall value and for most practical purposes can be ignored.

It is important that we note at this stage, that the accuracy of a sampling procedure depends both upon the distribution of the replicate results obtained (precision) and upon the presence of any bias. It is, however, common in a sampling specification to assume that the prescribed method is unbiased, and thereby accuracy and precision become identical. If we assume that all the results obtained lie within a normal distribution pattern, then we can express precision as indicating those results which make up 95% of the statistical sample (i.e. which lie within approximately ± two standard deviations from the mean value). Thus, if we specify precision as being twice the standard deviation, then under unbiased conditions:

Accuracy = 2 x (standard deviation).

At some point we must ask ourselves: ‘How many analyses must be performed on a given population for the overall error to lie within some estimated limits?' Remember that analyses are expensive and often labour intensive, and thus both the customer and the analyst will want the number kept to the minimum needed to assume the desired accuracy.

One of the main differences between the principles of sampling and of analytical determination is how we approach the question of error. The analyst is used to precise and generally reproducible techniques for performing an analysis, whereas the sample will often have to be taken from extremely variable material over which the analyst has no control. The sampling error therefore is generally much larger than the analysis error. The sampling error cannot be eliminated entirely, only reduced, either by the use of improved sampling techniques or by taking larger samples. It is therefore necessary for us to define maximum limits for sampling error, and to be able to work within these limits.

Let us suppose that as a result of making 30 determinations on a single lot of material, the value of the standard deviation for the component analysed was 0.187. If we set the maximum allowable difference between the estimate E and the actual value as 0.15, we can now calculate from equation 8 the approximate number of samples that we need to take.

From equation 6 we see that,

$$n=\left[\frac{ts}{E}\right]^2 \qquad (8)$$

From table 7, when the number of determinations exceeds 15, the value of t at the 95% confidence level is approximately equal to 2.

$$n=\left[\frac{2 \times 0.187}{0.15}\right]^2 = 6 \text{ or } 7 \text{ samples (probe)}$$

Therefore, for samples of a similar type to that use to determine the standard deviation, we need to take seven samples in order to ensure the required sampling accuracy is attained.

7 MONITORING THE PERFORMANCE OF ANALYTICAL PROCEDURES

An analytical laboratory should have, as one its principal objectives, the production of high-quality analytical results. This can be achieved by using of accurate and reliable analytical methods, which are appropriate for the analysis being carried out. However, experience has shown that deficiencies may occur when insufficient care is taken, either with the choice of an analytical method or with its application. The growing concern with poor laboratory practices has led to a proliferation of laboratory accreditation programmes, government regulations relating to good laboratory practice, and the development and application of quality control and quality assurance programmes. The common purpose of all of these is to ensure the accuracy, precision, and reliability of analytical results.

Various definitions have been suggested for quality control and quality assurance. Frequently the terms are used interchangeably. Quality Control can be defined as a planned system of activities, the purpose of which is to secure a product of defined quality. Quality assurance can be defined as a planned system of activities, the purposes of which is to provide assurance that the quality control programme is really "effective". Every quality assurance programme must have a set of objectives. The objectives will vary from one laboratory to another and will focus largely on the purposes for which the laboratory exists. Now although it is not the purpose of this Unit to consider in detail quality assurance programmes they will relate partly to calibration procedures. Examples are:

- adequate accuracy and precision of data generated by analysts within a laboratory;
- identification of weak methodology;
- ensuring that the analytical work will withstand legal scrutiny in any regulatory action.

Some of the ways in which these objectives can be realised are considered in the section below.

7.1 Use of Reference Materials and Certified Reference Materials

A Reference Material is a material or substance, one or more properties of which are sufficiently well established to be used for calibration purposes. When the value of that property has been certified by a technically valid procedure, and the sample of the material or substance is accompanied by a certificate or other documentation, the material can be defined as a Certified Reference Material.

Reference materials need not be pure single substances. They may be in the form of mixed gases, liquids, or even simple manufactured objects. To achieve certification the materials may either be analysed individually or be related to representative samples taken from a batch.

The certified value given for the material is often based upon results obtained from a number of laboratories, different methods of analysis being applied. Some of the results obtained for the material analysed may be rejected on the grounds that they differ sufficiently from those obtained from other laboratories. The certified value is thus the mean of the accepted results.

Reference materials are widely used by analytical laboratories:

- to calibrate analytical instruments,
- to validate analytical methods,
- to allow for the transfer of analytical results between laboratories.

Certified reference materials for calibration purposes are normally used when it is difficult for us to produce reliable standards. This may often occur when solid or gaseous matrices are involved. For instance, solid samples are regularly analysed by optical emission spectroscopy, and thus solid standards are required for calibration. Certified reference materials are available not only in a range of matrices, but also containing different quantities of analyte. Before we can transfer analytical results between laboratories, and be confident of the results we are providing, we must be prepared to carry out some check on our analytical methods by using an independent standard. A certified reference material of the type already indicated would serve to justify the reliability both of the method and the results supplied.

7.2 Requirements for a Standard Method of Analysis

Although it is difficult to define precisely what is meant by a standard method of analysis, the requirements of the method can be listed in order that it may be designed as standard:

- The method is known to be widely applicable to the analyte, present in a range of matrices.
- The method has been validated through inter-laboratory collaborative studies and is known to give accurate results.
- Interference effects are well documented.

The method requires only the use of normal equipment which would be found within the average analytical laboratory.

7.3 Assessment of Analytical Performance

In considering both reference material and standard methods of analysis, we have introduced the terms collaborative study and inter-laboratory study as the most effective way of guaranteeing the performance of a method or the results of an analysis. Both these terms represent forms of comparative study.

There are three ways in which a comparative study may be carried out:

- Between analysts, i.e. by intra-laboratory comparison,
- Between laboratories, i.e. by inter-laboratory comparison,
- Comparison between methods.

The comparison of different methods of carrying out an individual analysis can form part of either an intra- or an inter-laboratory comparative study. Let us now consider these terms in a little more detail.

7.3.1 Intra-laboratory comparison

Intra-laboratory testing provides a continuing assessment of the performance of both individual analysts and of laboratory instrumentation. Allowing two or more analysts to analyse the same sample by either the same or different procedures will help to identify any individual bias in the way in which a method is carried out, or to identify flaws in a given procedure.

When the results of an analysis are likely to form part of a litigation issue, then it is essential that the sample is analysed by two methods usually based upon different physical principles.

7.3.2 Inter-laboratory comparison

Inter-laboratory testing, sometimes termed proficiency testing, is a programme of work whereby a single sample (or possibly a number of samples) is analysed in a number of different laboratories. The main objectives of the programme are:

- to provide a measure of the precision and accuracy of the analytical method as applied in different laboratories,
- to estimate the accuracy and precision of results between laboratories,
- to identify weak methodology,
- to detect training needs,
- to upgrade, if necessary, the overall quality of laboratory performance.

The testing programme should have a co-ordinating organization that provides the sample to be examined by the participating laboratories. These samples are generally homogenous, in order to avoid any sampling errors, and the analytical procedure to be followed may also be specified.

Collaborative testing is a special form of inter-laboratory testing. This type of testing is used to evaluate an analytical method under real working conditions. All the participating laboratories follow the same procedure, and analyse portions of carefully prepared homogeneous samples.

8 Remediation of Contaminated Groundwater

8.1 General overview

Groundwater is an extremely important source of water. In many countries a major quantity of drinking and irrigation water is obtained from groundwater sources. Groundwater is also a significant provider of various environmental services. There are complex links between groundwater and surface water resources, which means that changes in either water quantity or quality may in turn affect the other. In addition, together with human and technological development, came a greater use and exploitation of water resources, many times without any kind of organization or sustainable use. As a consequence, instances of groundwater have become contaminated and effects can be felt on human health, becoming clear that the remediation of these aquifers is crucial in order to protect not only human health but also the environment.

Usually, the need for remediation actions is established based on the results of groundwater monitoring programs. If results indicate that groundwater contain contaminants at concentrations that make it a threat either to human health or environment, then groundwater may need to be remediated. In this sense, remediation is a broad term that refers to the reduction of risk caused by exposure to contaminated groundwater (Delleur, 2007).

Even though the cleanup goal may vary from site to site, restoration of groundwater until drinking water standards are met is currently the primary driver of groundwater remediation activities. However, groundwater remediation until achieving maximum contaminant levels may be impossible at many sites and extremely costly even when possible. On the other hand, even when strict cleanup goals are not technically achievable, their existence may provide an incentive against further pollution and may encourage development of cleanup technologies that better protect human health (NRC, 1994). Figure 17 shows a range of possible groundwater remediation goals and the text below briefly explains them.

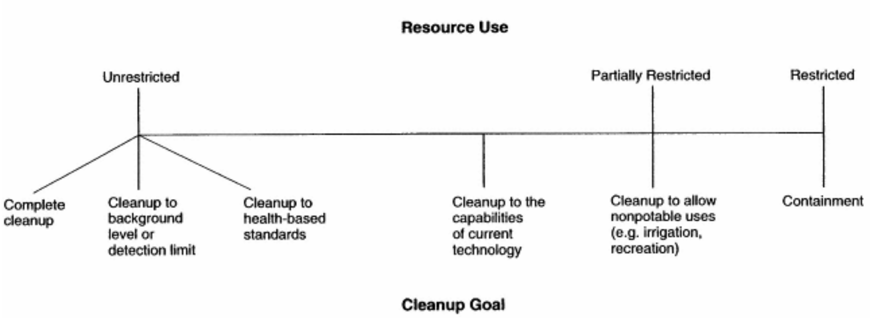


Figure 17 – Range of possible groundwater remediation goals. Source: NRC (1994).

The range of unrestricted remediation goals is composed by complete cleanup, cleanup to background level or detection limit and cleanup to health based standards.

A complete cleanup involves removing the contaminants in the aquifer to zero concentration levels. It is a groundwater remediation goal intended to provide the responsible entities with a continuous incentive to exercise care in handling wastes and to ensure that the most thorough cleanup possible occurs. However, the attainment of zero contaminant as an outcome for groundwater remediation should be recognized as an unattainable goal no matter how far cleanup technologies advance in the future, since even pristine waters contain certain inorganic chemicals regarded as contaminants. Additionally, limitations in analytical detection do not allow proving zero concentrations.

The use of background concentrations or analytical detections limits involves removing contaminants that exceed either one of them. This approach may be selected in cases where there is a naturally occurring concentration of a contaminant. Otherwise, analytical detection limits serve as cleanup goals, both cases with the advantage of eliminating the need for governmental agencies to define explicitly an acceptable risk level. Another benefit comes from the fact that remediation is kept up with the latest technologies. However, this type of remediation may have an elevated cost, representing a major drawback, along with the possibility that these goals will achieve only a small additional benefit, at a substantially higher cost, when compared with remediation to specific health based goals. Another drawback of this approach is that detection limits change over time as technology improves, meaning that remediation standards become outdated.

Health based goals can be set by two mechanisms. The first consists of removing eventual contaminants present at a concentration that could cause adverse health effects, using as standard for instance maximum concentration levels defined on legislation. The second refers to the use of risk assessments defined at each site.

The advantages of using predetermined standards instead of site specific risk assessments include speed and ease of implementation, consistency in the treatment of similar sites, usefulness for initial screening of contamination to determine its significance and avoidance of a need for technical expertise on the part of regulators in order to address toxicological and risk assessment issues on a case by case basis. Using predetermined standards, when established based on the "worst case" will also ensure adequate margins of safety for all sites. The most important drawback of using predetermined standards is the inability to account for site specific exposure patterns, which may result in higher expenditures than are necessary to protect public health at a particular site. Still, it is important to realize that groundwater remediation to assure a safe drinking water supply may not result in full restoration, as levels of contaminants may remain at concentrations greater than background levels. Further, contaminant levels designed to protect human health may not protect ecological receptors, which means that separate risk-based goals may be needed for ecosystem protection (NRC, 1994).

Partially restricted groundwater remediation goals include clean up to capabilities of current technology and cleanup to allow non potable uses. Under this scenario, remediation goals would correspond to the expected use of water and can be based on predetermined standards, such as water quality criteria or site-specific risk assessments.

Technology based goals specify a corrective action to be taken instead of a concentration to be reached. Even though best available technology may be unable to achieve concentrations based on health risk or may achieve concentrations below those necessary for public health protection, this type of approach as the advantage of avoiding raising false expectations about what level of cleanup is possible. Regarding drawbacks, they are related to a possible elimination of the incentive to develop technologies capable of reaching health based goals. When rigidly applied, this approach has the disadvantage of a possible overlooking of important site specific factors that could affect both implementation risks of that technology, and the ability of the technology to achieve actually the desired remediation at a particular site (NRC, 1994).

The last groundwater cleanup goal is containment, an approach according to which some established areas are allowed to remain degraded, as long as measures are taken to contain the contamination or to prevent public exposure by other means. Engineered systems can be used to prevent migration of the contaminants to locations where receptors could be exposed to them, which constitute a major drawback. Restricting groundwater use is particularly difficult when the contaminated water serves as a drinking water supply. In order to prevent exposure in these situations, there are three possible options: wellhead treatment, point of use treatment and development of alternative water supplies. Naturally, each one of these possibilities as limitations and their application depends on site specific conditions, as for instance, the availability and size of a municipal supply system or the proximity or existence of an alternative water source.

When it comes to the selection of a remediation goal, the degree to which groundwater can actually be remediated should be examined. However, above all, it is a political process which involves debates and several factors. Among these, issues like health risks and costs have received the most attention. Still, policy makers are becoming increasingly aware of the ecological risks of contamination and taking them into account.

After selecting a remediation goal, the next step consists of its implementation, in order to achieve the goal. Generally, groundwater can be remediated through one of the following three manners (Delleur, 2007):

- Containment - controlling a plume of contaminated groundwater involves preventing the plume from migrating to a location where receptors can be exposed to it. Techniques used to contain a groundwater plume include physical barriers (such as cut-off walls) or hydraulic barriers (like trenches or wells);

- Extraction - for some remediation approaches, groundwater must be extracted, either to allow ex situ treatment or to provide hydraulic control of contaminated groundwater. These types of systems are a combination of both subsurface and above the ground features.

- Treatment – contaminated groundwater can be treated, either in situ (e.g. bioremediation) or ex situ (e.g. biological processes), using a variety of physical, chemical or biological methods.

The next sections briefly describe the referred processes, as well as other techniques that fit into the previous cited categories.

8.2 Hydraulic containment of groundwater

8.2.1 Physical barriers

Even thought there are many alternatives for providing hydraulic containment of groundwater, the most widely used features are physical barriers and hydraulic barriers.

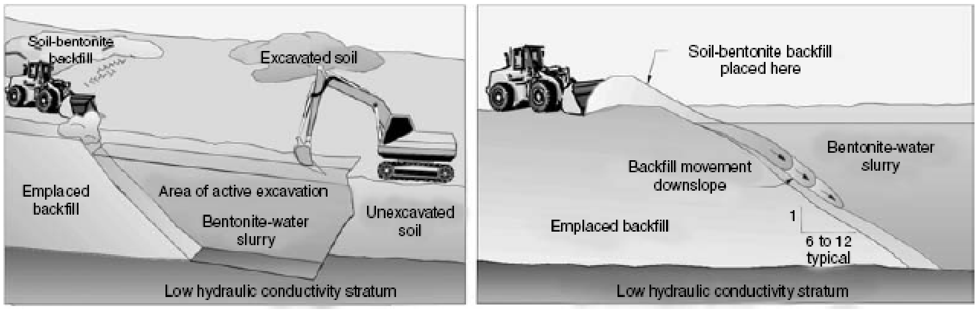
Physical barriers are vertical features in the ground that provide a barrier to groundwater flow. They can be formed using a variety of materials and can be either non selective (i.e., a barrier to the flow of all groundwater) or selective (i.e., a barrier to only the migration of target contaminants).

The most commonly used types of non selective physical barriers are cut-off walls. These devices limit the migration of groundwater by forming a physical impediment to groundwater flow. The effectiveness of the wall is a function of its continuity, resistance to degradation by contaminants in groundwater and to physical degradation. Because these barriers impede groundwater flow, the elevation of groundwater may rise on the up gradient side of the barrier. According to Delleur (2007), other controls may be needed in order to prevent overtopping or flanking of the barrier by contaminated groundwater, such as either groundwater extraction wells or trenches adjacent to the barrier to route mounded groundwater to a discharge point or permeable segments in the barrier to allow water to pass through controlled locations in the wall.

Another common type of physical barrier used in geotechnical and environmental remediation projects are slurry walls. The construction of these features consists of installing a mixture of soil, or other material and bentonite into a vertical trench to form a barrier to groundwater flow. The permeability of this vertical barrier is very low.

Figure 18 shows a very general approach to the construction of slurry walls, which includes (Delleur, 2007):

- Excavation of a narrow wide vertical trench. If the unsupported trench could cave, then the trench should be temporarily supported by using a bentonite slurry;
- Placing the soil bentonite mix in the slurry filled trench in a manner that displaces the bentonite slurry and forms a continuous vertical wall of low permeability soil-bentonite slurry. Typically, the soil-bentonite mix contains about 2% – 4% of bentonite clay, 20 – 35% water, 15 – 40% soil and about 2 – 4% of coarse material.



Overall operation

Backfilling schematic

Figure 18 – Soil bentonite slurry wall construction. Source: Delleur, (2007).

Generally, the material excavated from the trench can be used as the soil component of the soil-bentonite mix. When selecting a source of soil to use in the mix, issues like the grain distribution of the soil, treatment and disposal costs for excavated contaminated trench soils and the chemical composition of the soil should be considered.

Regarding the effectiveness of a soil-bentonite wall in preventing flow through the wall, it depends of the environment of the wall (i.e., the nature of groundwater constituents to which the soil-bentonite mixture is exposed to), the percentage of bentonite clay used in the soil bentonite mix, the type and gradation of soil used and finally, the quality of wall construction.

Monitored natural attenuation is an example of a selective physical barrier and involves the evaluation and monitoring of naturally occurring processes that prevent the migration of contaminants to receptors. Currently, it is most frequently used to describe biodegradation of contaminants by naturally occurring microorganisms, but other natural physical or chemical processes, like adsorption for instance may also effectively prevent the migration of contaminants. Under this approach, natural forces act on the contaminated groundwater without any human intervention, in order to remediate groundwater. Due to the presence of microorganisms in nearly all aquifers and because other naturally occurring processes like complexation or precipitation can migrate groundwater by attenuating contaminants, these naturally occurring processes can have a beneficial impact on groundwater quality (Delleur, 2007). A key component of this approach is a groundwater monitoring program that will allow verifying that natural processes are indeed resulting in the required degree of attenuation. Monitored natural attenuation can be used alone, as well as a supplement of conventional remediation techniques.

8.2.2 Hydraulic barriers

The term hydraulic barrier is used to describe a feature that causes a depression in the piezometric surface of groundwater and acts as a barrier beyond which groundwater within the zone of influence of the barrier should not flow (Delleur, 2007). Hydraulic barriers may be formed using groundwater collection trenches and groundwater extraction wells, which are the most common types of this kind of barriers.

Groundwater collection trenches can be installed in an aquifer to produce an induced hydraulic barrier by depressing the potentiometric surface of the aquifer. Figure 19 shows a typical groundwater extraction trench system.

During the design of a groundwater extraction trench system, the identification of the depth to which the trench must be constructed to induce a hydraulic barrier should be carefully selected, based on consideration of the seasonal variations in the elevation of groundwater, the location of contaminants and their depth in the aquifer.

Groundwater extraction wells can also be installed in an aquifer to induce a hydraulic barrier to groundwater flow. In fact, because most groundwater plumes are located at depths or in locations where collection trenches are not practical, groundwater extraction wells are more commonly used (Delleur, 2007). Figure 20 shows an example of a typical groundwater extraction well. The radius of influence and depth of influence of a single well can be calculated based on the properties of the aquifer, the geometry of the well and the pumping rate of the well.

When compared to well to extracting groundwater trenches may be more cost-effective than wells if contaminants are located at a shallow depth below ground (less than 15m) an the aquifer materials are relatively easy to excavate (Delleur, 2007).

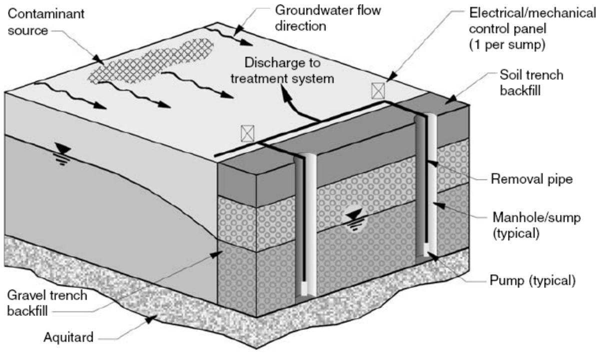


Figure 19 – Schematic representation of a groundwater extraction trench system. Source: Delleur (2007)

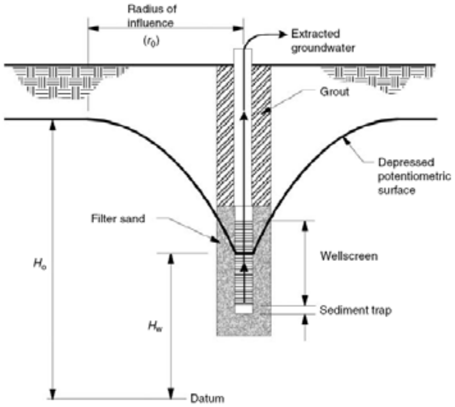


Figure 20 – Representation of a groundwater extraction well. Source: Delleur (2007)

8.2.3 Other approaches

In the past years, several alternative approaches to hydraulic containment have been developed. Some promising approaches are pointed out by several specialized authors.

Horizontal drains induce a barrier to groundwater flow in a manner similar to trenches. The accuracy of placing wells horizontally has improved considerably, mainly due to the recent advances in directional drilling technology. These features may be mostly useful in locations where access for excavation of a trench is not available, as for instance beneath a roadway.

Geomembranes can be incorporated into vertical barriers to provide an extremely low permeability barrier to groundwater flow. They offer excellent compatibility with subsurface contaminants and have highly uniform properties. In order to the barrier perform correctly joints between adjacent geomembrane panels must be carefully made so that leaks at these locations can be prevented.

Wellpoints are groundwater extraction devices that are typically driven into the ground. These features are useful in aquifer formations where a filter pack is not needed and where groundwater is at a relatively shallow depth. Generally, groundwater is extracted by suction or by using air lift techniques from wellpoints.

8.3 Groundwater extraction systems

Groundwater extraction systems are a combination of both subsurface features, like wells or trenches that provide access to contaminated groundwater, and above ground features that are used to regulate and monitor the extraction process.

8.3.1 Groundwater extraction well systems

Extraction well systems contain pumps, power sources and controls that are needed to actually remove the contaminated groundwater from the aquifer and transmit it to the treatment or disposal system. The next figure shows a typical groundwater extraction system.

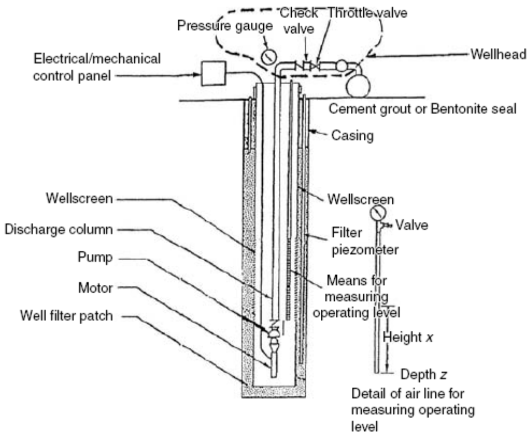


Figure 21 – Typical groundwater extraction system. Source: Delleur (2007).

These systems present some typical features. The next paragraphs present a brief description of each and one of these features.

The well is intended to provide access to the groundwater in the aquifer. The pump is used to raise groundwater from the aquifer to the above ground wellhead assembly. This feature, together with the motor, should be selected according to specific operating operations that exist during groundwater extraction and are related to flow extraction. The wellhead is the above ground assembly that contains the features necessary to transfer groundwater from the extraction well to the transmission piping. Some common components of the wellhead assembly include valves, fittings, flowmeters, pressure gauges and sampling ports (Delleur, 2007). Depending on the use of the area that surrounds the well, the wellhead can be either in an above ground shed or in a below ground vault. Transmission piping is a feature used to transmit the extracted groundwater from the wellhead to the treatment discharge location.

The power source is needed for the operation of the extraction system components. Power can be provided, for instance, by electricity or solar gas and local building codes should be checked to identify any specific requirements of the electrical system. Groundwater extraction systems are also equipped with a control panel containing all the electrical controls, like alarms for example, needed for the extraction system. Functions generally controlled at the panel include pump cycle time, pump temperature, monitoring for alarm conditions and transmission of data collected at the wellhead to a central processing unit. Finally, the discharge point is the feature at which the extracted groundwater is transferred to either the treatment system or the ultimate discharge point.

8.3.2 Groundwater extraction trench systems

A groundwater extraction trench system consists of the pumps, power sources and controls that are needed to actually remove the contaminated groundwater from the trench. These systems present some typical features, which are briefly described below.

Trenches are used for the extraction of groundwater and may be installed using one of the several methods available. Among these are, for instance, trench machines that install the pipe in a single operation. Backfill materials used in most types of groundwater extraction trenches include collection of piping and aggregate, materials which should be designed to resist degradation by chemicals in groundwater that they are exposed to. Features like pumps, transmission piping, power source, control panel and discharge point should be addressed as described on the previous section.

8.3.3 Other approaches

In addition to vertical wells trenches there are a several of groundwater extraction approaches available not only for removing groundwater but also to enhance the extraction of contaminants from the subsurface. Some of the more promising and innovative approaches to enhance extraction efficiency include, according to Delleur, (2007):

- Pneumatic hydraulic fracturing - fracturing subsurface media using water pressure or explosives to increase the permeability of the media and groundwater extraction efficiency;

- Flushing - re-injecting treated groundwater upgradient of the source area to increase the hydraulic gradient toward the extraction feature;

- Surfactant flushing or chemical extraction – flushing using surfactants or other chemicals that are designed to increase the mobility or solubility of contaminants in the aquifer;

- Electroacoustical decontamination – use of electrokinetic and acoustical waves to reduce surface tension and viscosity of separate-phase contaminants, increasing their mobility and opportunity to extract them;

- Steam extraction – injection of steam into the aquifer either to decrease the viscosity of a contaminant or to volatilize contaminants.

However, care should be taken when it comes to evaluating re-injection techniques that involve the use of chemicals, as they may pose a potential adverse impact either to human health or the environment.

8.4 Treatment of contaminated groundwater

There are quite many techniques available for the treatment of contaminated groundwater. These technologies can be characterized either as in situ, generally intended to either render a contaminant nontoxic trough treatment, or ex situ techniques that can only be used to treat groundwater that has been extracted from the aquifer.

8.4.1 In situ treatment

In situ techniques can be divided into three categories that incorporate biological processes (e.g. bioremediation), volatilization processes (e.g. soil vapour extraction) and chemical or physical processes (e.g. permeable reaction barriers). The next paragraphs present a short description of these techniques.

In situ bioremediation involves creating conditions in the subsurface that promote the growth of microorganisms that can degrade contaminants. The use of this methodology in groundwater remediation has increased in the last decades, as it exploits the capabilities of naturally occurring subsurface microorganisms, which can derive energy and often reproduce while metabolizing contaminants. Biodegradation reactions may involve destruction of organic contaminants, such as fuel hydrocarbons and chlorinated solvents, but can also involve transformation of inorganic contaminants to less toxic or immobile forms (e.g. nitrate to nitrogen gas). In situ bioremediation also involves the perfusion of treatment agents that stimulate biological growth and catalyze biodegradation reactions. Bioremediation agents can include edible organic substrates (e.g. soybean oil, ethanol, and molasses), air, oxygen gas, hydrogen gas, nutrients (nitrogen and phosphorus), wood mulch, specialized bacterial cultures and vitamins. These agents can be delivered either via batch-type injections into the subsurface or groundwater recirculation type designs (Delleur, 2007).

Naturally there are various and diverse types of bacteria present of the subsurface, and many of these microorganisms possess the capability to degrade common groundwater contaminants, like fuel hydrocarbons or nitrate. Many organic contaminants, such as polycyclic aromatic hydrocarbons and fuel hydrocarbons are degraded by the process of heterotrophic metabolism, in which bacteria use the contaminant as an electron donor and gain energy for maintenance and growth via microbial respiration. The by-products of complete biodegradation include carbon dioxide, water, and biomass. Biodegradation of synthetic organic contaminants in the subsurface may occur in a series of several steps, in which a contaminant is degraded into intermediate products before it is completely degraded. Bioremediation is often most successful in aquifers that are contaminated with chemicals that are easily metabolized by the indigenous microorganisms; in general, the more closely a contaminant resembles a naturally occurring compound, the more likely it is that there exists a microorganism in the aquifer that is capable of biodegrading the contaminant (Delleur, 2007). However, it is important to notice that the ambient conditions within the aquifer play an important role on the potential success of a bioremediation process.

Volatilization is defined as the transfer of a chemical from the liquid state to the gaseous state. Bioremediation techniques that employ volatilization processes promote the change of contaminants from liquid phase to the vapour phase. Generally, contaminants in the vapour phase are easier to remediate then those on the liquid phase, since aquifer materials are significantly more permeable to vapours easier to remove from the aquifer.

Remediation techniques that use volatilization processes include both soil and vapour extraction, which is applicable to contaminants adsorbed to soil in the vadose zone, and air sparging that is applicable to both dissolved and adsorbed contaminants in the saturated zone. Both processes are based in the principle of molecular diffusion of contaminants from the dissolved or non aqueous phase to the vapour phase. The range of chemical and physical processes often used to promote in situ treatment of contaminated groundwater include reduction with chemical reducing agents (e.g. sodium dithionite), reduction with zero-valent iron and chemical oxidation with permanganate. For a chemical process to be carried out to a high rate of completion, groundwater must be well mixed with reagents, which can be difficult to achieve in heterogeneous formations, low permeability formations and large plumes. Still, under some conditions, in situ chemical and physical treatment of contaminated groundwater is possible, particularly in situations where contaminated groundwater can be both directed to a collection point before it is treated and well mixed with treatment reagents. Chemical processes that can be considered for in situ application include adsorption, precipitation, oxidation/reduction, fixation and physical transformation. Such processes can be promoted either by installing a permeable reaction barrier in the aquifer to intercept contaminated groundwater and provide a controlled environment for the reaction or by applying reagents directly to groundwater trough wells or by infiltration from ground surface (Delleur, 2007).

8.4.2 Ex situ treatment

Ex situ biological processes refer to the treatment of extracted groundwater in vessels until the concentration of the contaminants is below a predefined level. These processes include, among others, bioreactor and slurry phase treatment.

In the first approach, bioreactor, contaminants are degraded by placing them in contact with microbes in an environment where biological growth is promoted. This can be achieved using either suspended (activated sludge) or attached (rotating biological contractors or trickling filters) growth systems. The microbial population can be either derived from the contaminated groundwater or added to the system. As for slurry phase treatment, extracted groundwater is mixed with soil and nutrients and they routinely agitated in a controlled environment to promote biodegradation of the contaminants. Typically, the slurry is placed in a lined area and left until the desired degree of biodegradation occurs. At least, the slurry is dewatered, and then the water and soil (both should be uncontaminated after biodegradation is completed) are properly disposed as non hazardous wastes. When compared to each other, this process offers much better control of process variables than the bioreactor approach, but it is slow and requires a larger area for implementation (Delleur, 2007).

9 Data presentation and analysis

The presentation of data from monitors and its availability for subsequent reprocessing if required is essential to the well being of the monitoring system. Without this the system may be thought not to be cost effective and adequate maintenance and resources may not be made available as required.

Data graphical presentation is required to observe the performance of the system and assist with maintenance. Graphical data is often preferable for managers to quickly observe trends and problems. In the past this would have been provided by chart recorders, but such records were often physically too large and could not compensate for calibration, cleaning and were not ideal for presentation to managers. Computer systems permit the reorganization of data in a presentable form free from irrelevant data.

In this chapter, an approach to Geographical Information Systems is made, in order to understand how this tool can help to better comprehend the results of monitoring programs. Monitorization is also addressed as a core part of Decision Support Systems.

9.1 Geographical Information Systems

Geographical Information Systems (GIS) have been rapidly developing in the last years, becoming powerful computer tools for varied applications, from sophisticated analysis and modelling of spatial data to simple inventory and management.

GIS can be described as a computer software and hardware for storing, manipulating, analysing and displaying spatial or geographically referenced data. GIS include cartographic tools that allow data display and generate professional-quality, publication-ready maps. Another GIS feature the capacity to create and manage geodatabases and datasets, providing a strong tool for storing and manipulation spatial information, as well as spatial data and associated descriptive information.

As a visualization tool, GIS allows graphical display of maps, tabular information, statistical analysis and modelling solutions. The spatial nature and analysis functions of GIS allow manipulating multiple themes of spatial data to perform operations such as overlay analysis, proximity analysis, surface analysis, and raster processing and conversion.

A great advantage of GIS is their ability to perform complex spatial analysis in a fast and cost effective way when compared to manual methods, representing a great benefit in planning scenarios or decision models as well as other problems requiring refinements to successive analysis.

Another advantage of using GIS is its visualization capability. Visualization is a way of interpreting an image in digital format and improving perception. Advances in GIS technology have been enabling an easier and more accurate visualization of the phenomena in a 3D environment, providing new opportunities for diverse types of analysis and data exploitation. Typical 3D visualization examples in groundwater engineering include visualization of contaminant transport, plume movement and delineation of remediation areas. GIS also allows producing maps and images.

Even though software and hardware are essential components of a GIS, data are by far the most important, as it allows users to perform analysis, visualization and modelling. Nowadays GIS allow using non spatial data with spatial indexing, as well as spatial data. If in the early stage of GIS implementation users had to develop spatial data by digitalizing or scanning paper maps, today many countries have started to develop national, regional or even local projects in order to provide digital data sets. The introduction of relational and spatial database management systems also posed a major evolution step to GIS data model. Maintenance of meta data (data describing other data) is an essential aspect of successful GIS projects.

For an effective management of groundwater it is necessary to develop an information system, together with a solid data base, that allows storing, understanding and administrating the data collected through the monitoring programs, described on the previous sections of this book.

GIS have been increasingly applied for geohydrologic research studies as they provide a variety of spatial analysis tools for groundwater modelling. GIS is one of the most important tools for integrating and analyzing spatial information from different sources. It helps to integrate, analyze and represent spatial information and database of any resource, which could be easily used for planning of resource development, environmental protection and scientific researches and investigations.

Developing a high-quality and useful GIS for groundwater management starts with a proper organization of relevant data and information. Different spatial data about the groundwater resource can be integrated into GIS systems, including the geological environment, aquifer system characteristics, well location and its characteristics, abstraction rates and water quality conditions of the study area.

GIS technology also helps to organize several data and to understand their spatial association. It is a strong analysis tool, that also synthesizes large amounts of information. Common examples of GIS applications in the field of groundwater include mapping information such as aquifer type and material, water table depths, aquifer recharge, managing site inventory data, estimating groundwater vulnerability, modelling both groundwater and contaminant movement, tracking particle movement, evaluating soil salinity and salt loading into groundwater and integrating groundwater quality assessment models with spatial data to create spatial decision support systems. GIS also allows interfacing with groundwater models, as for instance MODFLOW, making it easier to investigate environmental contamination, for instance.

9.2 Groundwater Decision Support Systems

Increasing public debate on water quality issues has added extra pressure on water quality monitoring and assessment process. Even though monitoring consists of measurements of a specific set of variables at one or more locations, over a given period of time, according to predefined schedules both in space and time, a monitoring program must be more than just data collection, and it involves other essential activities such as analysis and interpretation of data as well as the communication of results using an appropriate format for intended users.

Water quality monitoring, as already mentioned, can evaluate the physical, chemical and biological characteristics of a groundwater body in relation to human health or designated environmental values. Theses assessments are generally made by comparing data from monitoring programmes to water quality guidelines, water quality objectives or water quality targets. Water quality information can also be used for several other purposes, such as to determine sources of pollution (establishing cause and effect relations), regulatory purposes, to provide input for management tools like models and to support scientifically based decisions for preserving or improving the quality of a groundwater resource.

Governmental authorities are forced by law to make decisions within the framework of European, national and regional directives in the fields of spatial planning, groundwater and environmental protection. These tasks can be supported by a decision support system (DSS), which integrates data from various sources and helps to make decision processes more effective and transparent.

DSS are generally intended to generate alternative solutions to spatial problems and allow decision makers to use their judgement to choose from the alternatives. As human often make decisions that are limited by their knowledge of the environment, DSS strive to provide the decision maker with a broader spectrum of alternatives to help in the decision making process, usually by incorporating modelling within their framework, in order to answer “what if” type of questions. Generally, DSS become a necessity when some of the following problems arise:

- Uncertain evaluation: lack of information, complexity of system;
- Number of criteria: conflicting objectives and interests;
- Heterogeneous solution possibilities;
- Trans-disciplinary and complex problem situation, which cannot be managed by single person or single group of persons;
- Fast decisions for complex problems.

However, specific goals vary from one DSS to another, depending on the case study being addressed. Generally, DSS can be developed over a GIS base framework and thus incorporating geographical information. Another important component of DSS are data bases, as they contain all the needed information to manage the system. This information can be originated on the groundwater monitoring programs.

The first step in a DSS design and application is to define the nature of the problem and the purpose of the system. Although this may seem obvious, it is in important first step that is sometimes overlooked in a rushed effort to take action. As a part of DSS, selecting the appropriate model is essential for the system to succeed. The formulation of a conceptual model is required prior to the development of a mathematical model. In formulating a conceptual model, it should be an analysis of which processes are important in the groundwater system being investigated for the particular problem in study. The appropriate dimensionality and resolution of the numerical model should be selected, in order to address processes at a correct scale of study.

Development simulation models involves selecting or designing spatial grids and time increments that will yield an accurate solution for the given system and problem. There should be a specification of the properties of the system (and their distributions), stresses on the system (such as recharge and pumping rates), boundary conditions, initial conditions (for transient problems), and geochemical processes/reactions (if appropriate). All of the parameter specifications and boundary conditions must be consistent with the overall conceptual model of the system, and the initial numerical model reflects the analyst’s conceptual model of the system.

A model is a simplified approximation of a complex reality, but the model should capture the essential features and processes relative to the problem at hand. The selection of the appropriate model and appropriate level of model complexity (or, rather, simplicity) remains subjective and dependent on the judgment and experience of the analysts, the objectives of the study, the level of prior information available for the system of interest, and the complexity of the system being modelled. The trade-off between model accuracy and model cost will always be difficult to resolve, but will always have to be made. Water managers and other users of model results must be made aware that this trade-offs and judgments have been made and may affect model reliability (Delleur, 2007).

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ANNEX 2 – First Workshop Programme

FRAMEWORK PROGRAMME 6 – MARIE CURIE ACTION – ToK

The project

"DEVELOPMENT OF STRATEGIC ACADEMIA-INDUSTRY PARTNERSHIP IN ROMANIA FOR KNOWLEDGE MANAGEMENT

IN ENVIRONMENTAL FRIENDLY TECHNOLOGIES"

Acronym: KnowEnTech

The contract number: MTKI-CT-2005-029758

RESEARCH INSTITUTE FOR ELECTRICAL ENGINEERING

- ICPE SA -

POLITEHNICA University of Bucharest

WORKSHOP

ENVIRONMENTAL FRIENDLY TECHNOLOGIES

18 February 2009

Preamble 10:00 – 10:30 Presentation of ToK-KnowEnTech project during the third year

Prof. Dr. Aurelia Meghea - project coordinator

10:30 – 11: 00 Environmental monitoring of outdoor pollution parameters

Patricia Terceiro – LNEC, Lisbon, Portugal

11:00 – 11:30 Environmental friendly technologies in renewable energy systems

Dr. Ionel Popa

11:30 – 12:00 Coffee break

12:00 – 12:30 Conversion of solar and wind Energy

Dr.Virgil Racicovschi

12:30 – 13:00 Electronic and electric wastes

Dr Ionel Popa

13:00 – 13:30 Impact of emerging nanotechnologies on environment and health

Prof. Dr. Aurelia Meghea, Prof. Rodica Ceclan

13:30 – 14:00 Ground water monitoring according to Water Framework Directive

Patricia Terceiro – LNEC, Lisbon, Portugal

Location: ICPE SA, Splaiul Unirii 313, Setor 3, Bucharest

Contact informations: phone / fax: 4023907, 3154193 - UPB

Additional informations: phone / fax: 0215893316 - ICPE SA

ANNEX 3 – Second Workshop Programme

FRAMEWORK PROGRAMME 6 – MARIE CURIE ACTION – ToK

The project

“DEVELOPMENT OF STRATEGIC ACADEMIA-INDUSTRY PARTNERSHIP IN ROMANIA FOR KNOWLEDGE MANAGEMENT

IN ENVIRONMENTAL FRIENDLY TECHNOLOGIES”

Acronym: KnowEnTech

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RESEARCH INSTITUTE FOR ELECTRICAL ENGINEERING

- ICPE SA -

POLITEHNICA University of Bucharest

WORKSHOP

DEVELOPMENT ACADEMIA-INDUSTRY PARTNERSHIP IN FRIENDLY ENVIRONMENTAL TECHNOLOGIES

25 February 2009

Preamble 10:00 – 10:30 Industry-academia opportunities offered by for collaboration ICPE

Dr.Virgil Racicovschi

10:30 – 11:00 Presentation of research and technical activity of LNEC

Patricia Terceiro – LNEC, Lisbon, Portugal

11:00 – 11:30 Impact of partnership developed in KnowEnTech project

Prof.dr. Aurelia Meghea

1130 – 1200 Coffee break

12:00 – 12:30 Thermal comfort index for workers heath safety

Dr.Virgil Racicovschi

12:30 – 13:00 Waste waters under biological treatment

Dr Ionel Popa

13:00 – 13:30 Modern methods of effluent treatment

Patricia Terceiro – LNEC, Lisbon, Portugal

13:30 – 14:00 Prostects for Romanian-Portuguese industry-academia partnership

Prof. Dr. Aurelia Meghea

Location: ICPE SA, Splaiul Unirii 313, Setor 3, Bucharest

Contact informations: phone / fax: 4023907, 3154193 - UPB

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ANNEX 4 – Presentation of the Paper

GROUNDWATER MONITORING

Patrícia TERCEIRO[1], João Paulo LOBO FERREIRA[2], Teresa LEITÃO[3], Aurelia MEGHEA[4], Rodica CECLAN[5], Mihail CECLAN[6]

Groundwater extraction provides an important source of water supply. However, human development has been causing major pressures over the aquifers, requiring the identification and monitoring of both water quantity and quality, in order to define management strategies directed to protect water resources.

The paper presents a general overview of groundwater monitoring techniques and a summary of sampling procedures, as a result of a joint collaboration between the National Laboratory for Civil Engineering in Lisbon and Research Institute for Electrical Engineering Bucharest, during the common activity developed in the European FP 6 project, Marie Curie ToK – IAP: KnowEnTech, MTKI-CT-2005-029758.

Keywords: Groundwater monitoring, pollution sources, Water Framework Directive (WFD), Groundwater Directive.

1. Introduction

In the last decades, groundwater role and importance has increased, with the aquifers being more and more recognized as an essential and valuable natural resource. Groundwater extraction through wells provides an important source of water supply, not only for drinking water, but also for other uses like agriculture or industry. However, human development has been causing major pressures over the groundwater resources (increase of water demand, pollution problems), which need to be identified and monitored, in order to define management strategies directed to protect water quality and to guarantee that water is used in a sustainable way.

At the European Union level, the need to protect groundwater has been highlighted with the publishing of important legislative instruments, like the Water Framework Directive (2000/60/EC) and, more recently, with the Groundwater Directive (2006/118/EC) on the protection of groundwater against pollution and deterioration. Both pieces of legislation refer to the need to monitor groundwater systems,

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in order to better understand their state and to define protection measures, maintaining the resources in a good state.

This paper presents a general overview of groundwater monitoring techniques and a summary of sampling procedures.

2. Pressures on Groundwater Resources

Pressures on groundwater resources have been increasing all around the world, mainly due to human activities and climate changes. Monitoring the aquifer characteristics is crucial for quantifying and understanding the consequences of these pressures.

Water pollution results on the loss of the actual or potential beneficial uses of water, and is caused by any change in its composition due to human activity. There are many specific causes for water pollution, which fit on one of these two broad categories: Point Pollution or Non Point Pollution.

Point-source pollutants in groundwater are usually found in a plume shape, where the highest concentrations of the pollutant are near the source (such as the end of a pipe) and diminish further away from the source. In this case, harmful substances can be emitted directly into the water body. Point-source pollution refers to contamination originating from a single tank, disposal site, or facility. Wastewater discharges, industrial waste disposal sites, accidental spills, leaking gasoline storage tanks, and dumps or landfills are examples of point sources.

Non Point pollution is characterized by the difficulty in finding specific discharge areas and for having a large and diffuse number of polluting points. This type of pollution is usually found spread throughout a large area. Some examples of non point pollution sources include runoff from agricultural and forestry land, storm water runoff from urban areas and discharges from on-site sewage disposal systems.

The identification of the pollution sources existing in a study area is fundamental, in order to recognize expected type of pollutants, a possible concentration range, and to define monitoring programmes and sampling procedures. This identification can be done using tools like land cover, land use and land occupation cartography. Geographic Information Systems (GIS) can also help to determine some characteristics of the case study area, and fieldwork provides an opportunity to validate and update the data contained in the cartography.

3. European Legal Framework

Even though the need to protect the European Union waters has been highlighted for more than two decades, the major step towards an integrated management of the water resources inside the community space was taken with the Water Framework Directive. WFD introduces an integrated approach, focused on protection measurements and it requires governments to take a new holistic approach to managing their waters.

In this context, and for the first time, groundwater has become a part of an integrated water management system, as it is included in WFD's river basin management planning. Milestones considering delineation of groundwater bodies, economic analysis, characterization of pressures and impacts, monitoring and designing of programmes of measures are clearly defined, aiming to achieve good quantitative and chemical status for all groundwater bodies by the end of 2015.

It is in the physical space of the river basin that changes resulting from pressures, caused mainly by human activities are felt, and where water quality and quantity issues should be addressed. It is also inside the river basin that management and planning measures should be defined. In the river basin area should be also implemented monitoring programs, required by the WFD, to examine coherently and comprehensively the state of the water bodies. Monitoring is, therefore, a tool to support decision making in the water resources management [3].

In order to understand the current status of the waters and to define measures to achieve the goals imposed by WFD, it's essential to develop a monitoring programme, also foreseen in the Directive. The Directive sets a five-class scale - high, good, moderate, poor and bad. Article 8 sets out the monitoring requirements for monitoring surface water, groundwater and protected areas, which "are required to establish a coherent and comprehensive overview of water status within each river basin district". Monitoring will provide the information needed to assess the state of the water environment, to manage pressures on the water resources, and to assess long term trends.

For groundwater, the programmes referred in WFD shall cover monitoring of the chemical and quantitative status. Once Member States have determined the current status of their water bodies, monitoring then helps Member States to track the effectiveness of measures implemented to clean up water bodies and achieve a good status. WFD specifies three types of monitoring [4]:

- Long term surveillance monitoring: provides a broad understanding of the health of water bodies and tracks slow changes in trends, such as those resulting from climate changes.

- Operational monitoring: focuses on water bodies which do not meet good status and on the main pressures they face. This type of monitoring allows tracking the effectiveness of investments and other measures taken to improve the status of water bodies.

- Investigative monitoring: when further information about surface water bodies is needed and that cannot be obtained via operational monitoring, including information on accidents.

In addition to these three main types of monitoring, Member States need to carry out more detailed analysis in areas that are protected for drinking water or for natural habitats and species.

The Directive 2006/188/EC on the protection of groundwater against pollution and deterioration (Groundwater Directive) establishes specific measures to prevent and control groundwater pollution and sets up criteria for the assessment of good groundwater chemical status and for the identification and reversal of significant and sustained upward trends, as well as for the definition of starting points for trend reversals. These criteria take into account local characteristics and allow further improvements to be made based on monitoring data and new scientific knowledge.

This Directive establishes threshold values for the pollutants, groups of pollutants and indicators of pollution which, if exceeded, will indicate that a given groundwater body is at risk. As a minimum, Member States must establish threshold values for: ammonium, nitrate, arsenic, cadmium, chloride, lead, mercury, sulphate, pesticides and derivatives, trichloroethylene and tetrachloroethylene.

4. Guidelines to delineate a groundwater monitoring plan

4.1. General considerations

Groundwater is used for a variety of purposes, including irrigation, drinking water supply and manufacturing. To verify if groundwater is suited for its use, it is necessary to develop an assessment of its quality, by collecting samples for subsequent analysis. These samples should be collected according to a monitoring plan, in order to give an accurate overview of the system being monitored. Figure 1 shows a flow diagram with the typical sequence of groundwater monitoring activities.

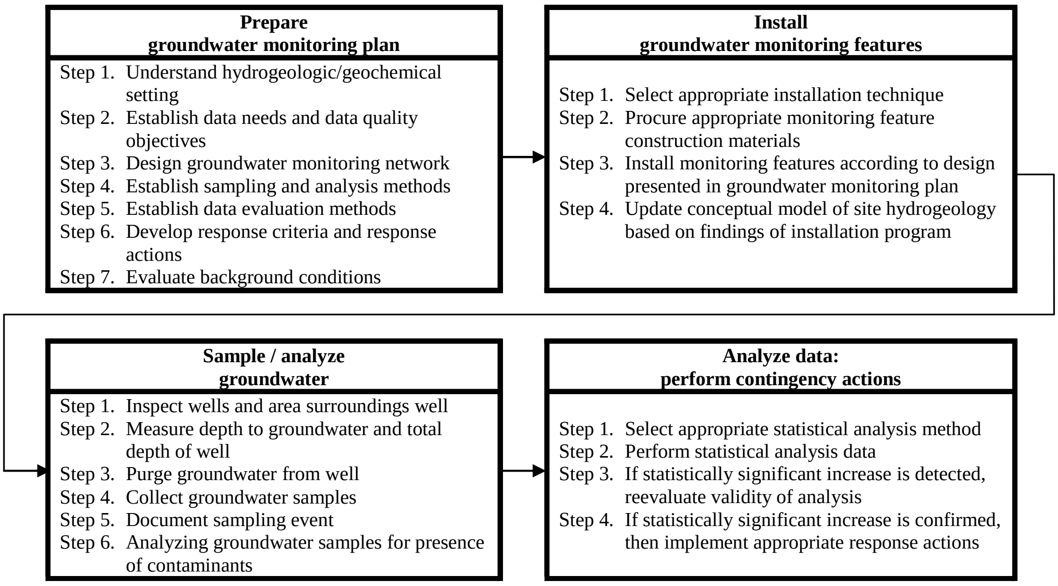

Fig. 1 – Steps to define a groundwater monitoring plan. Source: [2]

Developing a groundwater monitoring plan requires an in-depth understanding of site conditions, contaminant properties, regulatory requirements, and other technical considerations. An understanding of the factors that could affect the quality, validity or representativeness of groundwater samples is also essential.

It is recommended a step by step approach, as it helps to minimize errors and provides a clear and concise strategy to identify the goals, requirements, and limitations of the program. These plans ought to be able not only to describe each and every aspect of the groundwater monitoring, but also to control monitoring activities in order to guarantee that the overall goals of the groundwater monitoring strategy are fulfilled. A comprehensive and effective groundwater monitoring plan should address each activity that will occur during sampling analysis, data interpretation and response actions to be taken based on the results of monitoring [2].

The preparation of a groundwater monitoring plan begins with the understanding of the hydrogeological/geochemical setting. This knowledge is an essential prerequisite to design an effective groundwater system. This first information can be attained from available data from site explorations, literature reviews and previous experience with similar sites.

The type of data to be collected regarding the study area includes aquifer hydrogeological parameters (i.e., permeability, porosity, specific yield or specific capacity). It is also essential to have a geologic characterization of the site, as it is necessary to understand the main travel pathways expected for the contaminants if they were introduced into groundwater with certain characteristics of flow and transport.

Other examples of information that should be obtained before installing groundwater monitoring features include the limits of the aquifers, anisotropies in aquifer material, presence of discontinuities (e.g., fractures, solution cavities, channel deposits, etc.) within or between stratigraphic units or the surface topography of the site, as it may provide an indication of the potential impact of a contaminant release to groundwater, and also of the path these contaminants took until reaching an aquifer after being released from the ground surface. The interconnection between surface water and groundwater is another interesting issue for a more deep knowledge.

The purpose of groundwater monitoring is to define the water’s physical, chemical and biological characteristics within a certain site history which needs to be understood, and its aims should be defined before monitoring begins so that appropriate procedures, techniques, and analyses can be planned in order to meet the specific project needs.

4.2. Selection of the parameters to analyze

Parameter selection for chemical analysis is essential to the effective planning of sampling and analytical protocols. For exploratory efforts, it is useful to obtain slightly more chemical and hydrologic data than those required by the immediate information needs of the program. Nevertheless, these parameters should be targeted to give a general picture of the water quality and not a too detailed view. After these first results, then more specific parameters can be chosen to clarify exactly what are the parameters causing the global quality previously measured. The added data can normally be put to good use as the site conditions become better defined. For example, in a situation where essentially no chemical data exist for a site, a complete general mineral analysis should be included. The results provide an internal consistency check on major ionic constituents, field determinations, and the potential effects of unusually high levels of metals or nutrient anions. The results of the complete mineral analysis and field determinations define the major ion solution chemistry, which is quite valuable to obtaining an overall picture of the subsurface system of interest [5].

Having a complete mineral analysis and a clear view of information needs, it is possible to select any additional chemical parameters of interest. These parameters may be characterized as general groundwater quality parameters, pollution indicator parameters, and specific chemical constituents.

The process of selecting parameters should also consider eventual pollution sources present in the study area. Land use should be used to support this choice, as for instance, pollutants found in agricultural areas will necessary be different from those found in industrial or urbanized areas.

Table 1 contains an example of parameters that can be analyzed in groundwater sampling, as the final group should always be defined according to the above described. Regardless the amount of base information, the planning effort must incorporate flexibility to meet a variety of contingencies. The basis of a successful monitoring program is a robust, integral sampling protocol, coupled with proven analytical schemes.

Table 1- Example of groundwater parameters to analyse. Source: [6]

Measure in situ	*Chemical Analysis*	
Temperature	Total Organic Carbon	Cadmium
pH	Biochemical Oxygen Demand	Chromium
Redox Potential	Chemical Oxygen Demand	Lead
Electric Conductivity	Nitrate	Copper
Dissolved Oxygen	Total Phosphorus	Zinc
	Anions: Chloride, bicarbonate, sulphate	Iron
	Cations: Calcium, magnesium, sodium, potassium, manganese	

4.3. Groundwater monitoring points

Locating the appropriate monitoring point locations is fundamental in designing a monitoring network capable of providing data to achieve the program objectives. The preliminary locations and depths of monitoring wells should be selected on the basis of the best available pre-drilling data. Then, as the actual installation of these wells progresses, new geologic and hydrologic data should be incorporated into the overall monitoring plan to ensure that the finished wells will perform the tasks for which they are designed [5]. If wells or boreholes already exist on the field they can be included in the monitoring network, therefore reducing costs. However, it is important that they have good supporting geological information and construction details.

The density of monitoring wells should depend on the size and heterogeneity of the groundwater body, the geological and hydrogeological characteristics of the groundwater system, the aquifer vulnerability, and the risk posed to the aquifer from potential contaminant sources [1].

4.4. Sampling frequency

A possible approach to define sampling frequency can begin with a first evaluation of the type of source that is being monitored: a spill, slug, intermittent source, or continuous source. Then, it should be considered the likely pulse or continuous plumes of contaminants to be monitored, determine the minimum desired sampling frequency in terms of length along the ground-water flow path, and use hydrologic data to calculate the required frequency to satisfy these goals. However, ultimately, sampling frequency will result from a balance between the required number of samples to have representative data and the available budget [5].

In the initial monitoring phases, and whenever possible, it is recommended to perform more frequent measurements of the main parameters like pH, electrical conductivity, temperature, dissolved oxygen and redox potential, using proper devices. When quality trends are identified along a given period, it is possible to adopt a sampling frequency that better adjusts to the representative sampling collection [6].

4.5. Procedures to collect samples

A general approach to the sampling of groundwater monitoring wells should include a set of steps, for each monitoring point, including the localization and identification of the groundwater monitoring point, inspection of wells and surrounding areas, measurement of depth to water table and total depth of the well, collection of groundwater samples using appropriate techniques and, finally, measurement of physical-chemical parameters of the collected samples. The entire sampling event should be documented. All the material used in the field work should be properly prepared in the laboratory.

The monitoring plan should include a written protocol of the sampling procedures, including instructions and tasks to perform, as it follows [6]:

- Make a record of every sample collected and identify every bottle with a unique sample number, preferably by attaching an appropriately inscribed tag or label;
- Wash sampling devices with distilled water;
- Measure temperature, pH, electrical conductivity, redox potential, dissolved oxygen placing the electrodes submerged and about 2 cm away from the side and bottom of the water container; wait some minutes and register the parameter’s value;
- Wash the bottles at least twice with sampling water, unless they contain conservative substances or are sterilized;
- Collect the water sample directly on the bottle that will be transported;
- Use proper bottles according to the parameters that will be analyzed;
- Fill in a field report with sample identification, date and place of collection and parameters that will be analyzed.

Depending on determinations to be performed, the container may be totally filled (most organics determinations) or a space left for aeration, mixing, etc., for example for microbiological analyses;

For samples that will be shipped, it is recommended to leave an air space of about 1% of container capacity to allow for thermal expansion;

For samples containing organic compounds and trace metals special precautions are necessary, because of small concentrations (µg/l) of some constituents, they may be totally or partially lost if proper sampling and preservation procedures are not followed.

4.6. Equipment

Typically groundwater samples are collected in monitoring wells. However, piezometers and groundwater discharges can also be used to collect samples. Each feature has a purpose and a situation for which it is best suited.

Some groundwater monitoring programmes may include the use of direct monitoring devices, such as sensors or probes that allow analyzing groundwater quality in situ or on site. Multiparameter probes (Fig. 2) can be used for in situ measurements of the physical characteristics of water. These probes can be equipped with different electrodes, in order to monitor several parameters, like pH, conductivity or temperature. To guarantee the quality of the measurements, the electrodes should be calibrated with adequate standard solutions. These solutions are generally provided with the equipment, and each parameter as its proper type of solution.

Fig. 2 – Multiparameter probe

Fig. 3 – Sampling devices used to collect groundwater samples

Ion selective probes are another type of direct device commonly used at groundwater monitoring sites. These devices are designed to detect specific ions in groundwater, by producing an electric signal that can be compared to a reference signal for a specific ion constituent. This method is particularly useful for preliminary groundwater characterization and tracer studies.

Sampling devices (Fig. 3) are used to collect on point samples, representing water characteristics at the moment of collection.

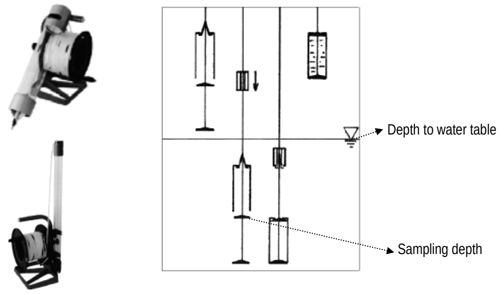

Fig. 4 – Groundwater sampling devices and schematic representation of its operation. Source: [6]

Fig. 5 – Diver operation. Source: http://www.surechem.com.my/

The procedure used to collect groundwater samples with this equipment consists on placing the device inside the monitoring point, at a given depth (Fig. 4). It is necessary to wait some minutes before collecting the sample, in order to restore water's natural circulation processes.

The diver (Fig. 5) allows automatic measurement and registration of groundwater levels and groundwater temperatures. This equipment can be installed on the monitoring well, suspended from a steel wire. Once installed, no part of the monitoring system should be left above the ground level, which reduces the risk of vandalism. The diver measures automatically both groundwater level and temperature, and registers these data in the internal memory, in a pre-defined time interval and for a certain period. This device needs to be programmed with location, starting time, rate, and measuring frequency. The data from the diver can be collected with a laptop.

Under certain circumstances, sampling can be an extremely hazardous operation. Safety harnesses and suitable protective clothing should be used when necessary, and often it is advisable that samplers should work in pairs for added protection.

4.7. Sampling conservation and storage

After the well has been sampled, the water must be properly transferred to the sampler container and preserved for the transport to the laboratory. During sampling, every effort must be made to minimize changes in chemistry of the sample, through a correct collection, preservation and storage.

The purpose of sample preservation is to minimize any physical, chemical, and/or biological changes that may take place from the time of sample collection to the time of sample analysis [7]. Three approaches (i.e., refrigeration, use of proper sample container, and addition of preserving chemicals) are generally used to retard volatile loss and chemical reactions such as oxidation, biodegradation and sorption.

Table 2- Summary of sample conservation processes. Source: [6] and [8]

Parameter	Type of container	Conservation	Maximum holding time
Solids	Plastic (polyethylene or equivalent) or glass	Refrigerate	7 days
Hardness		Add HNO_3 until pH<2	6 months
COD		Analyze as soon as possible or add H_2SO_4 until pH < 2; Refrigerate	7 days
BOD5		Refrigerate	6 hours
TOC	Glass	Analyze as soon as possible or add HCl until pH<2; Refrigerate	7 days
Metals (general)	Plastic (polyethylene or equivalent) or glass, rinsed with 1 + 1 HNO_3;	Add HNO_3 until pH<2	6 months
Oil and Fats	Glass wide-mouth Calibrated	Add H_2SO_4 until pH<2; Refrigerate	28 days
Total Hydrocarbons	Glass		
Nitrate	Plastic (polyethylene or equivalent) or glass	Analyze as soon as possible, Refrigerate	48 hours
Ammonia	Plastic (polyethylene or equivalent), teflon or glass	Add H2SO4 or HCl until pH<2 or Refrigerate	7 days
Total Phosphorus	Plastic (polyethylene or equivalent) or glass	Add H_2SO_4 or HCl until pH<2 or freeze without any additive	28 days
Sulphate	Plastic (polyethylene or equivalent) or glass	Refrigerate	28 days
Dissolved gases (O_2, CH_4, CO_2)	Glass	Dark	35 hours
Iron Manganese Sodium Potassium Calcium Magnesium	Plastic (polyethylene or equivalent) or Teflon	Add HNO_3 until pH<2	6 months
Phosphate	Plastic (polyethylene or equivalent), Teflon or glass	Refrigerate	35 hours
Chloride, Fluor			7 days
Silicate			7 days
Phenols	Teflon or glass	Add H_3PO_4 until pH<4 or Refrigerate	35 hours

The proper selection of containers (material type and headspace) is critical to reduce losses through several physical processes, such as volatilization, adsorption, absorption and diffusion.

All the sampling materials should be cleaned and quality assured before using. Table 2 presents an example for summary of sample conservation processes for a set of common groundwater parameters. Sample conservation refers to the actions taken to maintain sample quality during transportation.

Samples should be cooled to a temperature of 4°C (in insulated coolers) as soon as possible after they are collected and should be maintained at that temperature until they are received at the laboratory.

Nonetheless, even with proper preservation, no samples can be stored for an extended period of time without significant degradation. The maximum holding time is the period of time for which a sample can be stored after collection and prior to analysis (or pre-treatment) without the analytical results being significantly affected. Maximum holding time starts at the moment of sampling and ends with the beginning of the analytical procedure. Samples that exceed this period should be discarded, in order not to jeopardize data quality [7].

Each step of the sampling event should be recorded, including the time of sampling, weather conditions, time required to purge the well, volume of water purged, purge water characteristics, decontamination procedures, sample equipment calibration, and procedures for the preservation of samples [2]. These records should be kept for future reference.

5. Conclusions

WFD imposes EU Member states to develop monitoring programmes aiming not only to develop river basin management plans but also to define programmes of measures in order to achieve "good status" objectives by 2015. Regarding groundwater, these obligations concern chemical and quantitative status objectives.

Monitoring networks are a key feature to provide knowledge and understanding of the groundwater status, both at a river basin and regional scale. With this in mind, it is fundamental to develop strong and effective monitoring programmes, in order to define groundwater efficient protection and/or remediation measures.

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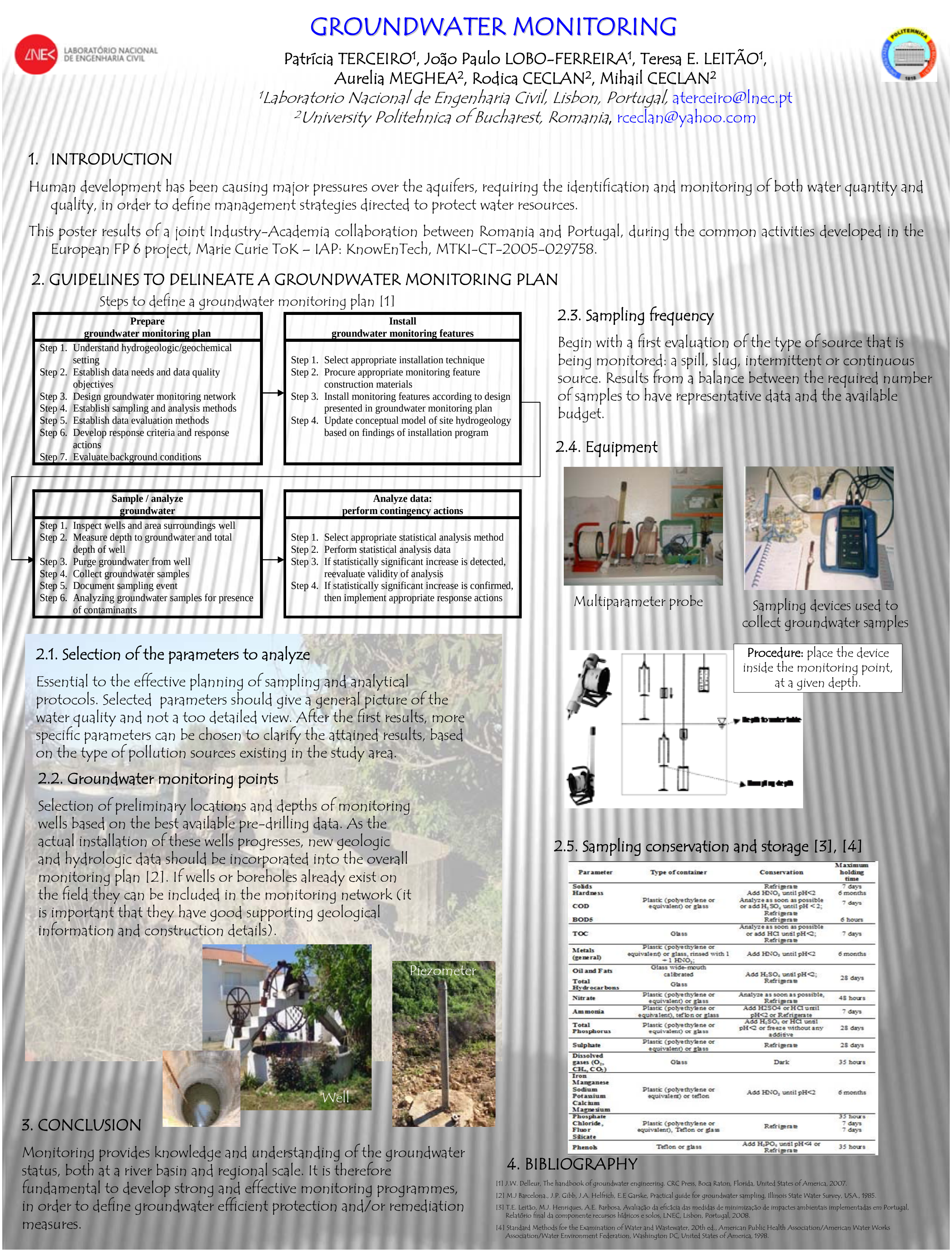
ANNEX 5 – Poster



GROUNDWATER MONITORING

Patrícia TERCEIRO[1], João Paulo LOBO-FERREIRA[1], Teresa E. LEITÃO[1],
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[2]*University Politehnica of Bucharest, Romania,* rceclan@yahoo.com

1. INTRODUCTION

Human development has been causing major pressures over the aquifers, requiring the identification and monitoring of both water quantity and quality, in order to define management strategies directed to protect water resources.

This poster results of a joint Industry-Academia collaboration between Romania and Portugal, during the common activities developed in the European FP 6 project, Marie Curie ToK – IAP: KnowEnTech, MTKI-CT-2005-029758.

2. GUIDELINES TO DELINEATE A GROUNDWATER MONITORING PLAN

Steps to define a groundwater monitoring plan [1]

Prepare groundwater monitoring plan

Step 1. Understand hydrogeologic/geochemical setting
Step 2. Establish data needs and data quality objectives
Step 3. Design groundwater monitoring network
Step 4. Establish sampling and analysis methods
Step 5. Establish data evaluation methods
Step 6. Develop response criteria and response actions
Step 7. Evaluate background conditions

Install groundwater monitoring features

Step 1. Select appropriate installation technique
Step 2. Procure appropriate monitoring feature construction materials
Step 3. Install monitoring features according to design presented in groundwater monitoring plan
Step 4. Update conceptual model of site hydrogeology based on findings of installation program

Sample / analyze groundwater

Step 1. Inspect wells and area surroundings well
Step 2. Measure depth to groundwater and total depth of well
Step 3. Purge groundwater from well
Step 4. Collect groundwater samples
Step 5. Document sampling event
Step 6. Analyzing groundwater samples for presence of contaminants

Analyze data: perform contingency actions

Step 1. Select appropriate statistical analysis method
Step 2. Perform statistical analysis data
Step 3. If statistically significant increase is detected, reevaluate validity of analysis
Step 4. If statistically significant increase is confirmed, then implement appropriate response actions

2.1. Selection of the parameters to analyze

Essential to the effective planning of sampling and analytical protocols. Selected parameters should give a general picture of the water quality and not a too detailed view. After the first results, more specific parameters can be chosen to clarify the attained results, based on the type of pollution sources existing in the study area.

2.2. Groundwater monitoring points

Selection of preliminary locations and depths of monitoring wells based on the best available pre-drilling data. As the actual installation of these wells progresses, new geologic and hydrologic data should be incorporated into the overall monitoring plan [2]. If wells or boreholes already exist on the field they can be included in the monitoring network (it is important that they have good supporting geological information and construction details).

2.3. Sampling frequency

Begin with a first evaluation of the type of source that is being monitored: a spill, slug, intermittent or continuous source. Results from a balance between the required number of samples to have representative data and the available budget.

2.4. Equipment

Multiparameter probe

Sampling devices used to collect groundwater samples

Procedure: place the device inside the monitoring point, at a given depth.

2.5. Sampling conservation and storage [3], [4]

Parameter	Type of container	Conservation	Maximum holding time
Solids	Plastic (polyethylene or equivalent) or glass	Refrigerate	7 days
Hardness		Add HNO_3 until pH<2	6 months
COD		Analyze as soon as possible or add H_2SO_4 until pH < 2; Refrigerate	7 days
BOD5		Refrigerate	6 hours
TOC	Glass	Analyze as soon as possible or add HCl until pH<2; Refrigerate	7 days
Metals (general)	Plastic (polyethylene or equivalent) or glass, rinsed with 1 + 1 HNO_3;	Add HNO_3 until pH<2	6 months
Oil and Fats	Glass wide-mouth calibrated	Add H_2SO_4 until pH<2; Refrigerate	28 days
Total Hydrocarbons	Glass		
Nitrate	Plastic (polyethylene or equivalent) or glass	Analyze as soon as possible, Refrigerate	48 hours
Ammonia	Plastic (polyethylene or equivalent), teflon or glass	Add H2SO4 or HCl until pH<2 or Refrigerate	7 days
Total Phosphorus	Plastic (polyethylene or equivalent) or glass	Add H_2SO_4 or HCl until pH<2 or freeze without any additive	28 days
Sulphate	Plastic (polyethylene or equivalent) or glass	Refrigerate	28 days
Dissolved gases (O_2, CH_4, CO_2)	Glass	Dark	35 hours
Iron Manganese Sodium Potassium Calcium Magnesium	Plastic (polyethylene or equivalent) or teflon	Add HNO_3 until pH<2	6 months
Phosphate Chloride, Fluor Silicate	Plastic (polyethylene or equivalent), Teflon or glass	Refrigerate	35 hours 7 days 7 days
Phenols	Teflon or glass	Add H_3PO_4 until pH<4 or Refrigerate	35 hours

3. CONCLUSION

Monitoring provides knowledge and understanding of the groundwater status, both at a river basin and regional scale. It is therefore fundamental to develop strong and effective monitoring programmes, in order to define groundwater efficient protection and/or remediation measures.

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