



# Universitat Autònoma de Barcelona - Facultat de Ciències Llicenciatura de Ciències Ambientals

# PROJECTE DE FINAL DE CARRERA 2011

# Ra isotopes and Rn as a tool for the water management resources: the Alberquillas Aquifer (Málaga-Granada)

JosepOriol López Plana

Directors: Dr. Jordi Garcia-Orellana Valentí Rodellas Vila

Quan surts per fer el viatge cap a Itaca, has de pregar que el camí sigui llarg, ple d'aventures, ple de coneixences. Has de pregar que el camí sigui llarg, que siguin moltes les matinades que entraràs en un port que els teus ulls ignoraven, i vagis a ciutats per aprendre dels que saben.

LLUÍS LLACH

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Primer de tot m'agradaria donar les gràcies al meu director de projecte, el Jordi Garcia-Orellana per haver-me donat la oportunitat de conèixer en el món de l'oceanografia de costa perquè estar qualsevol dimarts pel matí damunt d'una barqueta no té preu. Donar-te les gràcies per ensenyar-me tot el que he après en radioactivitat i el "Hola què tal?" que val molt!

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#### **PREFACE**

The aim of this project is to evaluate the importance of submarine groundwater discharge sector in order to improve the water balance in Málaga-Granada region. The approach of this study arose from the the geology and the aquifers that indicate that there could be some discharge to the sea between Maro (Málaga) and Almuñécar (Granada) and the Andalusian's Government and its Water Agence were really interested in evaluating it because there is a lot of population and few water available and the magnitude of groundwater discharge has generated controversy. Is well known that water is a scarce resource in this area and it's very important for the society and for the environment. The legislation, the water policies, the knowledge of the aquifer and the geology, the water dynamics, the land use and the water perception in the society might help the management of this resource not just in Andalusia but in all the Mediterranean basin.

The main objective is to evaluate the submarine groundwater discharge from the Alberquillas Aqufier to the sea by measuring <sup>222</sup>Rn and Ra isotopes. Specific objectives have been established to achieve the main objective:

- Reveal the importance of water resources in the Mediterranean basin.
- Learn radiometric techniques for the study of groundwater discharge to the sea.
- Learn of sampling techniques of water samples for the measurement of Ra and Rn.
- Learn the techniques for measuring Ra (RaDeCC) and Rn (RAD7).
- Interpretation and discussion of results.

During this semester, and in addition of the present study in Málaga-Granada region, the author has participated in the initial phase (sampling, analysis and interpretation of preliminary results) of other research projects focused on the study of submarine groundwater discharges through the use of Ra isotopes and <sup>222</sup>Rn. These studies have been developed in different areas, including Alt Empordà (Roses and Sant Pere Pescador), Maresme with CMIMA's group (Mediterranean Center for Marine and Environmental Research), Delta de l'Ebre, Peñíscola and Mallorca with the IMEDEA's group (Mediterranean Institute for Advanced Studies).

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# 1. INTRODUCTION

#### 1. INTRODUCTION

Water is one of the keys of development. Population in the Mediterranean basin is near the coast and next to the rivers and they use this resource for different uses like themselves (drinking, cooking, washing, etc.), agriculture, social habits... That's why the quality and the quantity of water is one of the main problems in the world. Rich countries have the ability to draw water from wells, move water from one side to another and even take water from the rain or the sea and purify it, but poorer countries aren't. That's why, UNESCO and European Union have created programs to ensure the availability of water in the Mediterranean basin.

But water management is not as easy as it seems, water management involves all the society beginning from the legislation and policies to the dynamical physics and hydrogeology. Thinking in water means sociology, health, laws, economy, negotiations, territorial planning, cartography, projects organisation, but also chemistry, termodynamics, physics, hydrology, geology, ecology (marine and terrestrial) and even maths! For this reason, all these subjects must be minded for a good water management.

#### 1.1. WATER MANAGEMENT

# 1.1.1. MANAGEMENT OF WATER RESOURCES IN THE MEDITERRANEAN BASIN

Water, from antiquity, was recognized as one of the vital elements of nature, an essential requirement for life and for any type of development. Today, the sustainable development of the Mediterranean region is the main objective of the governments looking after the environment. For that purpose the sustainable water management is required in order to ensure and guarantee equal access for all the people, under the recognition that "access to minimal clean water" is a fundamental right to ensure that water allocation and control strengthens the economic and social welfare in the region and to ensure environmentally water needed (Mar del Plata Action Plan, United Nations Water Conference, 1977, preamble; Agenda 21, United Nations Conference on Environment and Development 1992, chapter 18, para. 47). Water is an essential element impossible to replace, expensive to transport and store, and difficult to purify and has been always considered "valuable", but today, this scarce natural resource is under a particularly high pressure as a result of a combination of three factors: (a) rapid demographic changes, with permanent or seasonal increases in population, particularly in urban and coastal areas. (b) high consumption of water for irrigated agriculture and (c) water pollution and deterioration of water resources due to various anthropological interventions.

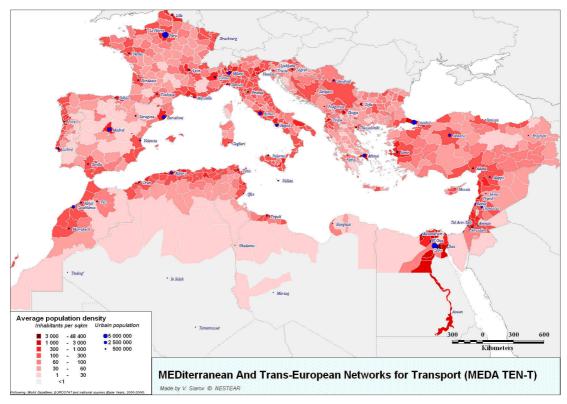


Figure. 1: Population density in the Mediterranean basin (IEMed, 2005).

Climate change may also add to the vulnerability of water systems and their complexity increasing the impact of the pressures indicated. Thus, in the Mediterranean basin there are three zones classified by the climate:

- 1. The eastern Mediterranean where climate is one of the most drier in the world.
- 2. The northern Africa where the total rain and its distribution is not homogeneous changing considerable in time, space and with the distance from the coast.
- 3. The European part of northern Mediterranean that has an abundance of water resources and a recharge through a sustained regular rainfall in most parts of the subregion that implies no shortage of water. All major hydrographic basins of the Mediterranean (except Nile River) are located in this subregion (Ebro, Rhone, Po and Neretva).

Due to geographic and climatic variations, as well as political and socioeconomic differences that characterize the various Mediterranean countries and subregions, there is a huge variation in the availability and access to water is showed.

Mediterranean sea presents significant disparities between the coastal area and inland region due to excessive population growth and coastal urban high demand for water (Figure. 1), which may not always be successfully provided by nearby sources. The seasonal increase in population due to tourism in many coastal areas (such as Camargue, Andalusia or Croatia) leads to a water crisis and a deterioration in the quality of it, particularly during late summer in several of these areas. The situation is particularly serious in countries (e.g. Middle East

countries) with low investment opportunities because they have no effective means to overcome the breakdown of water supply and its pollution.

For all these reasons, the European Union and the United Nations have created some programs for the water management in the Mediterranean basin, such as MEDA program, the Blue Plan or INECO.

# **MEDA Water Program**

The official name of the MEDA Water program is Euro-Mediterranean Regional Program for Local Water Management.

The program is part of the support of the European Union for the development of the water sector in the North African and Middle East (MENA) countries under the MEDA Regional Indicative Programming (Table 1). The available budget for MEDA Water is 40 M€. From this amount, nine different consortia of non-profit organisations (NGOs, Universities and Government Agencies) receive grants up to 5 M€ for the implementation of measures related to local water management.

The Program intents to improve local water management conditions through co-operation of non-profit organisations, capacity building, construction of demonstration plants, technology transfer and creation of awareness. It aims mainly at three technical components: (1) water supply and wastewater reuse (in agriculture and in an urban set-up), (2) irrigation water management and (3) improvement of decision-making structures in irrigation, rural water supply and sanitation, and drought management. (Table 2)

The MEDA program concludes that "encouraging results had been achieved in all sectors mentioned above. Successes could be reported in many fields: farmers increasingly manage their water resources themselves; villages are planning improvement of water availability and its use, and negotiate their investment needs with local, regional and national authorities; wastewater reuse is becoming more accepted through clear guidelines and pilot projects. North-South academic exchanges have taken place on a large scale on subjects such as drought management, wastewater treatment, wastewater reuse, autonomous desalination, irrigation technology, dissemination technology and others. The capacity of MENA countries to solve their problems has therefore increased. Due to this, the European Commission now considers to implement a follow-up phase of selected Program activities".

The eleven main projects of MEDA program (Table 3) might be explained for understanding the importance of water and its management tendencies in the Mediterranean basin.

Table 1: All the countries involved in the Meda Water projects (MEDA

program).

program).		
Name	Projects	
ALGERIA	EMWIS	
AUSTRIA	EMWIS, MEDWA, ZERO-M	
BELGIUM	EMWIS	
CYPRUS	EMWIS, MEDAWARE, MEDROPLAN	
EGYPT	ADIRA, EMPOWERS, EMWIS, ISIIMM, ZERO-M	
FINLAND		
FRANCE	EMWIS, ISIIMM	
GERMANY	EMWATER, ZERO-M	
GREECE	ADIRA, EMWIS, MEDAWARE, MEDROPLAN	
ISRAEL	EMWIS	
ITALY	EMWATER, EMWIS, IRWA, ISIIMM, MEDROPLAN, ZERO-M	
JORDAN	ADIRA, EMPOWERS, EMWATER, EMWIS, IRWA, MEDAWARE, MEDWA	
LEBANON	EMWATER, EMWIS, IRWA, ISIIMM, MEDAWARE	
LUXEMBOURG	EMWIS	
MALTA	EMWIS	
MOROCCO	ADIRA, EMWIS, ISIIMM, MEDAWARE, MEDROPLAN, ZERO-M	
NETHERLANDS	EMPOWERS	
PALESTINE	EMPOWERS, EMWATER, EMWIS, MEDAWARE, MEDWA	
PORTUGAL	EMWIS	
ROMANIA		
SLOVENIA		
SPAIN	ADIRA, EMWIS, IRWA, ISIIMM, MEDAWARE, MEDROPLAN, MEDWA	
SYRIA	EMWIS	
TUNISIA	EMWIS, MEDROPLAN, ZERO-M	
TURKEY	ADIRA, EMWATER, EMWIS, MEDAWARE, ZERO-M	
UNITED KINGDOM	EMPOWERS	

Table 2: The different Areas of Action of the Meda Water Program (MEDA

program).

AreasOfAction	Description	Projects		
I	Integrated management of local drinking water supply, sanitation and sewage.	EMPOWERS, EMWATER, MEDAWARE, ZERO-M		
II	Local water resources and water demand management within catchment areas and islands.	EMPOWERS, IRWA, ISIIMM, MEDWA		
III	Prevention and mitigation of the negative effects of drought and equitable management of water scarcity.	EMPOWERS, MEDROPLAN		
IV	Irrigation water management.	EMWATER, IRWA, ISIIMM, MEDWA		
V	Use of non-conventional water resources.	ADIRA, EMPOWERS, MEDAWARE, MEDROPLAN, MEDWA, ZERO-M		
VI	Preparation of national and local scenarios for the period until 2025 for sustainable water management.	EMPOWERS, EMWIS, MEDWA		

Table 3: MEDA water projects (MEDA program).

	Table 3: MEDA water projects (MEDA program).						
Acronym	Countries	Themes	Coordinators				
ADIRA	EG, ES, GR, JO, MA, TR	V	George Papadakis				
	<b>Description:</b> Integrated management of local water supply and sanitation; wastewater reuse; use of non conventional water resources						
<b>EMPOWERS</b>	EG, GB, JO, NL, PS	I, II, III, V, VI	Peter Laban				
	<b>Description:</b> Improvement of decision-making in rural water supply and sanitation, and drought management						
EMWATER	DE, IT, JO, LB, PS, TR	I, IV	Ismail Al Baz				
	<b>Description:</b> Integrated management of local water supply and sanitation; wastewater reuse; use of non conventional water resources						
IRWA	ES, IT, JO, LB	II, IV	Maria Teresa Calabrese				
	Description: Irrigation water management						
ISIIMM	EG, ES, FR, IT, LB, MA	II, IV	Michel Soulié				
	<b>Description:</b> Irrigation water management						
MEDAWARE	CY, ES, GR, JO, LB, MA, PS, TR	I, V	Maria Loizidou				
	<b>Description:</b> Integrated management of local water supply and sanitation; wastewater reuse; use of non conventional water resources						
MEDROPLAN	CY, ES, GR, IT, MA, TN	III, V	Dunixi Gabina				
	<b>Description:</b> Improvement of decision-making in rural water supply and sanitation, and drought management						
MEDWA	AT, ES, JO, PS	II, IV, V, VI	Hanan Salah				
	<b>Description:</b> Irrigation water management						
ZERO-M	AT, DE, EG, IT, MA, TN, TR	I, V	Martin Regelsberger				
	<b>Description:</b> Integrated management of local water supply and sanitation; wastewater reuse; use of non conventional water resources						
EMWIS	AT, BE, CY, DZ, EG, ES, FR, GR, IL, IT, JO, LB, LU, MA, MT, PS, PT, SY, TN, TR	VI	Eric Mino				
	<b>Description:</b> EMWIS is an information and knowledge exchange tool on water among the Euro-Mediterranean Partnership countries						

- (1) The ADIRA Project: "Autonomous Desalination System Concepts for Sea Water and Brackish Water in Rural Areas with Renewable Energies Potential, Technologies, Field Experience, Socio-Technical and Socio-Economic Impacts" aims to develop suitable concepts and to install a number of desalination units around the Mediterranean, for fresh water supply in rural areas. In the focus of this project are environmental friendly, autonomous desalination units powered by renewable energy sources with fresh water output in the range of half to ten cubic meters per day. In the framework of the ADIRA project ten new desalination units were installed in Morocco, Jordan, Cyprus and Turkey. The experience and knowledge gained from planning, installing and monitoring the implemented technologies and from the evaluation of the potential of such systems, gives more light in the performance and cost issues of a clean but expensive technology.
- (2) The EMPOWERS Partnership is a regional partnership of 15 different national and international partners working together in Egypt, Jordan and Palestine to develop practical participatory methodologies that influence bottom up planning, and that lead to improved local water governance. Also working regionally, EMPOWERS supports a Regional Information Program to

disseminate the Partnership's work and create links with other actors involved in improving local water management across the region. The EMPOWERS Partnership is a 4 year program (2003-2007) that is mainly funded by the EC's MEDA Water Program with a total budget of 8.4 M€. Our main objective is to improve long-term access and rights to water and water related services by vulnerable populations in MEDA Zone through participatory water planning & management processes with all stakeholders.

- (3) EMWater: "Efficient Management of Wastewater, its Treatment and Reuse in the Mediterranean Countries" is a mainly EU-funded project that encourages reuse-oriented wastewater management. The EMWater project promotes innovative wastewater treatment and reuse solutions in its four partner countries Jordan, Palestine, Lebanon and Turkey through:
  - Trainings of staff involved in water resources management,
  - Development of a guide for decision-makers and water resources planning engineers,
  - Applied research and demonstration of innovative solutions by the implementation and operation of pilot plants, and
  - Dissemination and awareness raising activities.

Experts from the field, decision-makers, interested citizens, and civil organisations are involved in all stages of project implementation.

**(4) EMWATER:** "Efficient Management of Wastewater, its Treatment and Reuse".

Given the fact of water shortage crisis in the Mediterranean countries the EMWATER project aims to highlight innovative solutions in wastewater treatment and wastewater reuse. With this goal in mind experts from the field, decision-makers, interested citizens and civil organizations should be sensitized to these issues.

A more specific aim is the strengthening of regional co-operation through the creation of networks among the experts as well as through cross-border knowledge transfer. Additionally the project aims at strengthening capacity building through local and regional training programs, the development of regional policy guidelines for wastewater treatment and reuse in the region.

The improvement of the security and safety of water supply in the Mediterranean countries is the best recipe for social, economic and political stability in the region and is, thus, the foremost goal of the project.

- **(5) IrWa:** "Improvement of Irrigation Water Management in Lebanon & Jordan". It's objectives are improve irrigation water quality, increase crop production and farmers' income, improve on-farm irrigation and fertilization efficiencies and enhance flood prevention to increase the agricultural area.
- **(6) ISIMM:** "Institutional and Social Innovations in Irrigation Mediterranean Management". The overall objective is overcoming current contradictions associated with local water management in Mediterranean river basins through

innovative institutional solutions, based on common understanding of six key axes: social, institutional, territorial, historical, agricultural and hydrological-hydraulic.

**(7) MEDAWARE Project:** "Development of Tools and Guidelines for the Promotion of the Sustainable Urban Wastewater Treatment and Reuse in the Agricultural Production in the Mediterranean Countries".

The highest priority in the wastewater management sector in every country has to be given to setting up an effective wastewater management system which will include:

- Maximization of collection of wastewater,
- Upgrading the existing wastewater collection systems,
- Rehabilitation or upgrading of existing wastewater treatment plants or the construction of new treatment plants,
- Establishment of proper standards for influent and effluent wastewater quality,
- Education of the farmers.
- **(8) MEDROPLAN:** "Mediterranean Drought Preparedness and Mitigation Planning". The project contributes to the objectives of the MEDA WATER Program by enhancing regional co-operation in the areas of sustainable and integrated management of water resources. The objectives are:
  - Develop guidelines for drought preparedness plans that,
    - o Minimize the impacts of drought providing a risk management approach.
    - o Include the physical and socio-economic characteristics of Mediterranean countries.
    - Respond to the actual situation of institutional and civil stakeholders
  - Set up a drought preparedness network for the Mediterranean countries.
- **(9) MEDWA:** "Stakeholder Participatory Sustainable Water Management at farm Level". The project objective is strengthen the interactive stakeholder capacity in irrigation water management in Jordan & Palestine by:
  - Implementation of efficient water demand management.
  - Implementation of efficient water supply management
  - Establishment of effective fore for experience exchange to strengthen interactive stakeholder capacities in irrigationwater management.
- (10) The Ec'Eau Sebou project, financed by the European Union has been implemented by the Sebou Water Basin Agency (ABHS) and WWF-Mediterranean Program, with the support of ACTeon, an environmental consultant based in France. It aims at displaying the importance of economic approaches for integrated water resources management in Morocco. The project attempts to:

- Introduce the role of the economic methodologies and tools in integrated water resources management.
- Test economic analysis and tools in the Sebou basin.
- Draw lessons from these tests concerning the relevance of economic analysis methodologies and tools for water resources management in Morocco.

# (11) **Zer0-M:** "Sustainable Concepts towards a Zero Outflow Municipality Objective".

Zer0-M aims at concepts and techniques to achieve optimised close-loop usage of all water and nutrient flows in small municipalities or settlements including tourism facilities. Zer0-M is about abandoning the concept of waste water.

# **Blue Plan**

On the same direction but from another organisation, the Blue Plan is one of the stakeholders involved in the cooperation between the 21 states bordering on the Mediterranean and the European Community. This plan is an original mechanism for environmental regional cooperation within the framework of the United Nations Environment Program's Mediterranean Action Plan (UNEP/MAP). One of the main tasks is to produce information and knowledge in order to alert decision-takers and other stakeholders to environmental risks and sustainable development issues in the Mediterranean, and to shape future scenarios to guide decision-taking processes.

All of the Blue Plan's work is structured around its four main strategic objectives, which are:

- To identify, collect and process on an on-going basis environmental, economic and social information of use to the stakeholders and decisionmakers
- To evaluate the interaction between the environment and economic and social development in order to measure what progress is being made towards sustainable development
- To conduct analyses and prospective studies to help shape visions for the future and back-up decision-taking
- To broadcast and circulate products and outcomes in the manner bestsuited to the target public.

# **INECO**

INECO (Institutional and Economic Instruments for Sustainable Water Management in the Meditteranean Region) is a Coordination Action Project supported by the European Commission. The aim of INECO is defined as "to establish a Mediterranean network of research institutes, public authorities and stakeholders for coordinating research, and to analyse decision making practices regarding the application of institutional instruments in the water sector".

INECO encompasses a series of coordination activities aiming to:

- Promote the exchange and dissemination of best available water management practices through the systematic exchange of information and research among the participating parties and the consideration of institutional and socio-economic instruments improving sustainable, equitable and efficient water use.
- Perform studies for the assessment of the efficiency, effectiveness and equity of currently applied water management practices, as well as the role of public involvement in planning and implementing alternative actions.
- Promote capacity building for constructively engaged Integrated Water Resources Management, with emphasis on socio-economics and policy considerations.

# 1.1.2. MANAGEMENT OF WATER RESOURCES IN SOUTH-EASTERN SPAIN.

The hydric management is directly influenced by legislation. In Europe there is the "Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Comunity action in the field of water policy".

This Directive has as its object as it is stated, getting the good ecological and chemical status of all waters, continental, transitional, coastal and groundwater. In some ways, it is assumed that the most important issues related to the provision in Europe are well targeted. The main problems affecting the waters at this time are related to the quality of them, with consequent negative implications for both human health and aquatic ecosystems and rivers.

In terms of SGD, this Directive has a special interest because of the emphasis that it gives to the groundwater. In the introduction it ensures "The quantitative status of a body of groundwater may have an impact on the ecological quality of surface waters and terrestrial ecosystems associated with that groundwater body" and it talks about the desire of a good groundwater quality. On this way, the "Directive 2006/118/EC of the European Parliament and of the Council of 12 December 2006 on the protection of groundwater against pollution and deterioration" sets out principles and good statements for groundwater.

This policy gives more weight to integrate water planning with other environmental protection concepts, especially the figures of protected natural areas and gives priority to the establishment of participatory processes and public information plans during different stages of development.

In Spain, the Directive 2000/60/EC is transposed to the Water Law approved by Royal Legislative Decree 1/2001 of 20 July, whereby the process of water planning culminates with the publication of river Basin Management Plans of the various demarcations in December 2009.

In addition to the general objectives set out in the Water Law, Basin Management Plans should ensure the environmental objectives established in the art. 92 and 92 bis of the Water Law, that are:

For surface water (including transitional and coastal):

- 1. Prevent deterioration of surface water bodies.
- 2. Protect, improve and restore all surface water bodies in order to reach the good state.
- 3. Progressively reduce pollution and gradually eliminate discharges, emissions and losses of priority hazardous substances.

# For groundwater:

- 1. Avoid or limit the entry of pollutants into groundwater and prevent the deterioration of the of all groundwater bodies.
- 2. Protect, improve and restore bodies of groundwater and ensure a balance between the extraction and recharge in order to get good status of groundwater.
- 3. Progressively reduce the concentration of any pollutant resulting from human activity

This work focuses on two basins in Andalucia (Southern Spain): the Mediterranean Coast (called Sur) and the Guadalquivir's Basin (Figure. 2).

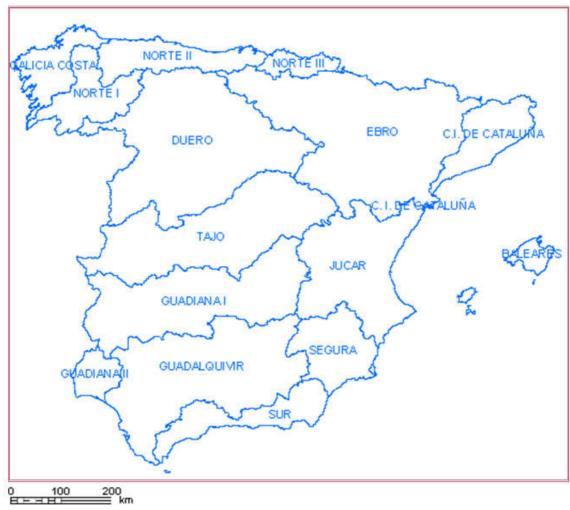


Figure. 2: The different basins in Spain. (Sistema de Información del Agua Subterránea. (IGME, 2002)).

Those two basins have Hydrological Plans but they are olders than the Directive 2000/60/EC. Another administrative problem is that those basins were Spanish Government competence but after the Directive implementation they became competence of the Andalusian Water Agency. So, they have to elaborate new plans but untill then, the ancient Hydrological Plans are valid. The new Basin Management Plans will have a wider focus than a management approach based largely on infrastructure work.

There are already experiences with planning and coordination at the subregional and sub-basins, such as Coordinated Plans.

Coordinated programs come from the initiative of social groups, environmentalists, neighborhood, government, etc. which are presented to the Parliament of Andalusia in the form of Proposal not of law. Once adopted, the Government of the Junta de Andalucía is asked to write a program that serves as an operational tool where the objectives and the most priority actions are established to achieve, as well as check its viability. The program is designed with a regional character that seeks the recovery and development of the basin, considering all the possibilities of water resources and optimization of operations, rationalization of water resources and environmental protection. In order to do this, agencies should constitute to ensure the management of water

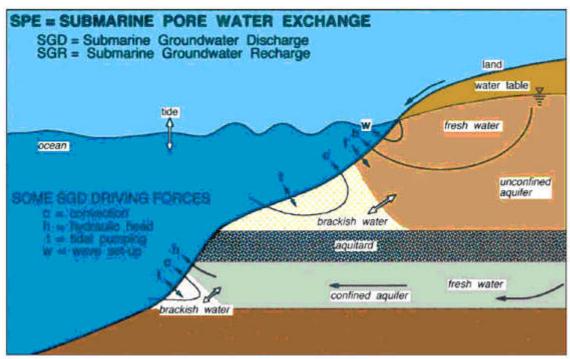
in the basin and the effective coordination of actions arising from the program and the participation of all stakeholders.

#### 1.2. SUBMARINE GROUNDWATER DISCHARGE TO THE SEA.

# 1.2.1. DEFINITION AND IMPORTANCE OF THE SUBMARINE GROUNDWATER DISCHARGE

Directive 2000/60/CE (Water Framework Directive) defines in the 2<sup>nd</sup> article that "Groundwater" means all water which is below the surface of the ground in the saturation zone and in direct contact with the ground or subsoil. Groundwater is recharge (infiltration from rainfall, runoff and evapotranspiration) and discharge as extractions anthropogenic sources, rivers, lakes and to the sea.

**S**ubmarine **G**roundwater **D**ischarge (SGD) is the flow of water through continental margins from the seabed to the coastal ocean, with scale lengths of meters to kilometers, regardless of fluid composition or driving force (Burnett et al., 2003). Flow may be induced by the terrestrial hydraulic gradient as well as by marine processes such as wave set-up, tidally driven oscillations, density-driven convection, and thermal convection (Figure. 4). The mix will be different in different regions, depending, for instance, on the hydraulic conductivity, hydraulic head, groundwater catchment area and recharge rates.



**Figure. 4:** Schematic depiction (no scale) of process associed with submarine groundwater discharge. Arrows indicate fluid movement. (Taniguchi, M. et al., 2002).

But, why is SGD important? SGD represents circa 5-10% of global freshwater sources to oceans, in the Atlantic total SGD (freshwater plus recirculated seawater) is up to 80-160% of the river flux entering the Atlantic Ocean (Moore et al., 2008), dissolved material transports is much more important that water itself and SGD may be a major pathway for micronutrients

(e.g. iron, molybdenum). In the Mediterranean basin, while the main rivers (Rhone, Po, Nile, Ebro, Tiber, Adige) discharge 158 km<sup>3</sup>/y, the freshwater SGD might be between 45 km<sup>3</sup>/y (Plan Bleu, 2003) and 68 km<sup>3</sup>/y (Zektser et al., 2007).

On one side, the flux of freshwater due to SGD may be important because it can represent an exploitable freshwater resource. Moreover, this flux constitutes a required parameter for the hydrological balances to be closed and, thus, an estimation that water administration agents and decision makers would make profit from. When considering discharging groundwater as an exploitable resource, this quantitative importance can be more or less restricted to some specific areas (e.g. karstic zones). Even though, a SGD flux estimation can be helpful in taking decisions on hydrological policies such as installation of desalinization plants in coastal areas or restrictions in groundwater exploitation in a given area.

On the other side, biogeochemical implications of SGD may go even farther. SGD could also drive an input of chemical compounds (nutrients, metals, etc.) into the coastal areas (Moore 1996; Rama and Moore 1996; Krest et al., 1999, 2000; Charette et al., 2001). These fluxes may affect the biogeochemical cycles of the sensitive coastal environments where they take place, likely inducing ecological effects like water eutrophication (Valiela and D'Elia, 1990). Many researchers have already recognized the biogeochemical importance of groundwater discharge through coastal sediments. Transport of nutrients to coastal waters may trigger algae blooms, including harmful algae blooms, having negative impacts on the economy of coastal zones (LaRocheetal, 1997).

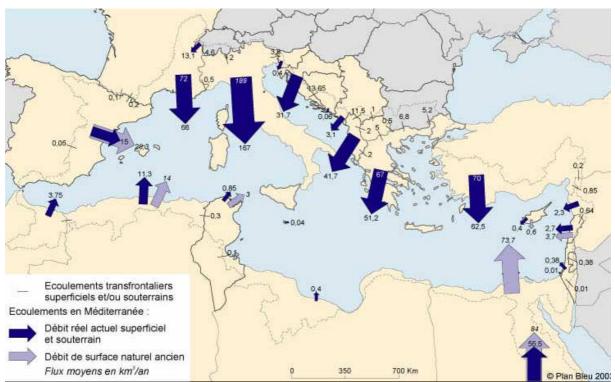


Figure. 5: Magnitude of SGD in each country of the Mediterranean basin. (Plan Bleu, 2003).

#### 1.2.2. DETECTION AND QUANTIFICATION

There are different methods in quantifying SGD

# (1) HYDROGEOLOGICAL MODELS

To understand the regulatory mechanisms of coastal systems and for a proper efficient management of water resources in areas like the Mediterranean Sea, characterized by a traditional lack of resources and high punctual demand, is necessary to establish the water balance, which involves a precise quantification of the different water flows.

A model can be understood as the representation of an object, process or real system. In hydrogeology, models are used with two purposes: firstly we use them to simulate a particular observed behavior and to predict how the flow system will behave in the future and secondly the models can be used to reproduce flow hypothetical situations and to understand as well the type of flow system we have (Anderson and Woessner, 1992). They are, therefore, a tool that allows a greater understanding of flow systems.

However, a model determines the mass balance of a system (inputs - outputs = change in mass) thus becoming an important tool for managing water systems. At the same time, models are instruments of integration as they allow to join a variety of information (geology, geophysics, geochemistry, etc.)..

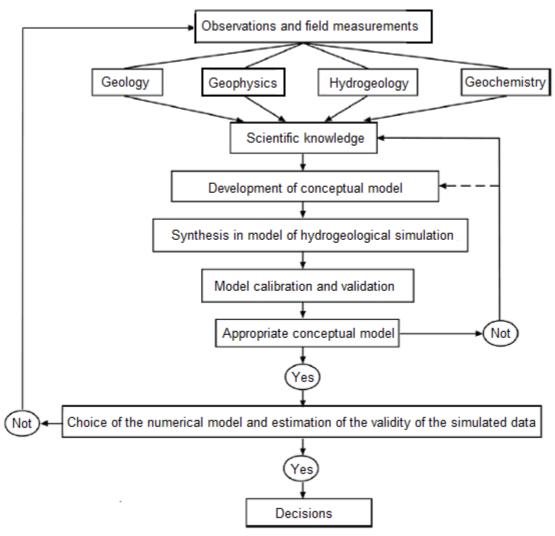
Groundwater models are usually applied to four types of problems:

- Groundwater flow.
- Transport of solute.
- Heat flow.
- Deformation of the aquifer.

In this work we are interested in studying the models that allow the estimation of the groundwater flow.

The development of a hydrogeological numerical model simulation is a sequential process that begins with developing a conceptual model that describes and explains the main features of the system. Conceptual models can be understood as a series of hypotheses that describe the geology, hydrogeology, and hydrodynamics of a system and how these are related and structured in order to know its effects on the flow phenomena. Numerical models are understood as the mathematical expression of this conceptual model.

Consequently, the elaboration of a conceptual model is necessary to define the geometry, the processes and the properties of the medium. However, there are many difficulties associated with the definition of these three parameters, such as knowing the geological contours and which will be the hydrogeological behaviour and knowing whether the properties can be thoroughly measured and are always reliable and representative. The level of detail required for the realization of a conceptual model not only depends on the type of problem to be solved (flow, transport or deformation) but also on the purpose for which the model has been developed (resource management, contaminated run-off study, hypotheses about operating flow systems, etc...)



**Figure. 3:** Flowchart identifying the steps involved in the development of a hydrogeological simulation model (Folch, A., 2005).

# (2) DIRECT METHODS

Seepage meters: Measurements of groundwater seepage rates into surface water bodies are often made using manual "seepage meters". Israelsen and Reeve (1944) first developed this device to measure the water loss from irrigation canals. Lee (1977) designed a seepage meter consisting of one end of a 208L steel drum that is fitted with a sample port and a plastic collection bag. The drum forms a chamber that is inserted open end down into the sediment. Water seeping through the sediment will displace water trapped in the chamber forcing it up through the port into the plastic bag. The change in volume of water in the bag over a measured time interval provides the flux measurement.

# Two-way valve with 0.9 cm inner diameter Threaded port End section of 55-gallon steel drum Seepage Sediment

Figure. 6: Sketch of a simple "Lee-type" manual seepage meter (Lee, 1977).

Other automatic seepage meters have been developed using the temperature gradient (Taniguchi and Fukuo, 1993 and 1996; Taniguchi and Iwakawa, 2001; Granier, 1985), absorbance measurements (Sholkovitz et al., 2003) or with ultrasonic measurements (Paulsen et al., 2001).

*Piezometers:* Another method for assessing groundwater seepage rates is the use of multi-level piezometer nests. With this approach, the groundwater potential in the sediments can be measured at several depths (Freeze and Cherry, 1979). Using observations or estimates of the aquifer hydraulic conductivity, one can then easily calculate the groundwater discharge rate into the ocean by use of a one-dimensional form of Darcy's Law (equation (1)):

$$q = -Kdh/dL \tag{1}$$

where q is Darcian flux (groundwater discharge volume per unit area per unit time), K is hydraulic conductivity, and dh / dL is the hydraulic gradient in which h is hydraulic head and L is distance.

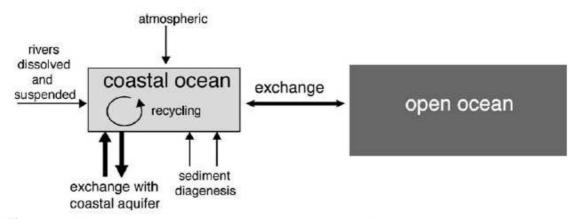
# (3) INDIRECT METHODS

Natural tracers: One approach for local to regional-scale estimation of groundwater inputs into the ocean uses naturally occurring geochemical tracers. An advantage of groundwater tracers is that they present an integrated signal as they enter the marine water column via various pathways in the aquifer. Although small-scale variability is a serious drawback for the use of seepage

meters or piezometers, such small spatial scale variations tend to be smoothed out over time and space in the case of tracer methods (Burnett et al., 2001a).

Natural geochemical tracers have been applied in two ways to evaluate groundwater discharge rates into the ocean. One approach is the use of geochemical tracers that are enriched in groundwater relative to the seawater. Then, the concentration of a solute in the receiving water body is attributed to inputs of that component derived only from groundwater (Moore, 1996; Cable et al., 1996a,b; Porcelli and Swarzenski, 2003). However, natural tracers require the evaluation of tracer sources and sinks, what always difficults the exercise. A second approach is the use of vertical profiles of the geochemical compositions in sediment pore waters under the assumption that its distribution can be described by a vertical, onedimensional advection—diffusion model (e.g., Cornett et al., 1989; Vanek, 1993). However, this is usually limited to the case of homogeneous media and thus, presents the same limitations as direct measurments methods.

Ideally, in order to provide a detectable signal, a groundwater tracer should be greatly enriched in the discharging groundwater relative to coastal marine waters, conservative, and easy to measure. Several tracers have been shown to meet these criteria fairly well: Over the past few years, several studies used natural Ra isotopes and <sup>222</sup>Rn to assess groundwater discharge into the ocean (Burnett et al., 1990, 1996; Ellins et al., 1990; Moore, 1996; Rama and Moore, 1996; Cable et al., 1996a,b, 2004; Moore and Shaw, 1998; Corbett et al., 1999; Hussain et al., 1999; Corbett et al., 2000; Moore, 2000; Krest et al., 2000; Charette et al., 2001; Kelly and Moran, 2002; Kim and Hwang, 2002; Burnett et al., 2002; Burnett and Dulaiova, 2003; Garrison et al., 2003; Krest and Harvey, 2003; Crotwell and Moore, 2003; Moore and Wilson, 2005). Radium isotopes and radon present several characteristics that may be exploited for groundwater discharge studies. In applying geochemical tracing techniques, several criteria must be assessed or defined, including boundary conditions (i.e., area, volume), water and constituent sources and sinks, residence times of the surface water body, and concentrations of the tracer. Sources may include ocean water, river water, groundwater, precipitation, in situ production, horizontal water column transport, sediment resuspension, or sediment diffusion. Sinks may include in situ decay or consumption, horizontal water column transport, horizontal or vertical eddy diffusivity, and atmospheric evasion (Figure. 7). Through simple mass balances or box models incorporating both sediment advection and water column transport, the geochemical approach can be quite useful in assessing SGD.



**Figure. 7:** Box model showing how radium isotopes can be used to investigate exchange between the coastal and open ocean (Moore, 1999)

Another approach consists of application of in situ gamma-ray spectrometry techniques that have been recognized as a powerful tool for analysis of gamma-ray emitters in sea-bed sediments, as well as for continuous analysis of gamma-ray emitters (e.g., <sup>137</sup>Cs, <sup>40</sup>K, <sup>238</sup>U and <sup>232</sup>Th decay products) in seawater (e.g., Povinec et al., 2001).

Methane (CH<sub>4</sub>) is another useful geochemical tracer that can be used to detect SGD. Rosenberg et al. (1988) and Cable et al. (1996a) found inventories of <sup>222</sup>Rn and CH<sub>4</sub> in the coastal waters varied directly with groundwater seepage rates and had a positive relationship. Bugna et al. (1996) demonstrated that groundwater discharge was an important source for CH<sub>4</sub> budgets on the inner continental shelf of the same region.

Several other natural radioactive (<sup>3</sup>H, <sup>14</sup>C,Uisotopes, etc.) and stable (<sup>2</sup>H, <sup>3</sup>He, <sup>4</sup>He, <sup>13</sup>C, <sup>15</sup>N, <sup>18</sup>O, <sup>87/88</sup>Sr, etc.) isotopes have been used for conducting SGD investigations, tracing water masses, and calculating the age of groundwater.

Some artificial tracers like anthropogenic atmospheric gases (e.g., CFC's) have been used to evaluate SGD.

In addition to geochemical tracers, geophysical tracers such as groundwater temperature can be used to estimate groundwater discharge rates. Two basic methods are used when using temperature as a tracer: (1) temperature-depth profiles under the assumption of conservative heat conductio-advection transport; and (2) temperature differences in the groundwater-surface water system as a qualitative signal of groundwater seepage using techniques such as infrared sensors or other remote sensing methods.

Water balance approaches: The water balance equation for a basin has also been used to estimate fresh SGD and may be described as follows:

$$P = E_{\rm T} + D_{\rm S} + D_{\rm G} + dS \tag{2}$$

where P is precipitation,  $E_T$  is evapotranspiration,  $D_S$  is surface discharge,  $D_G$  is fresh groundwater discharge, and dS is the change in water storage. Over extended periods (i.e., years), dS is usually assumed to be negligible. Therefore, one needs to know precisely the precipitation, evapotranspiration and surface runoff for an accurate estimation of  $D_G$  by this approach.

Basin-scale estimations of fresh SGD via a water balance method have been performed in many places, e.g., Perth, Australia (1.0×10<sup>8</sup> m³/year; Allen, 1976), Santa Barbara (1.2×10<sup>5</sup> m³/year; Muir, 1968), Long Island, New York (2.5× 10<sup>7</sup> m³/year; Pluhowski and Kantrowitz, 1964), and in the Adriatic Sea (1.7×10<sup>11</sup> m³/year; Sekulic and Vertacnik, 1996).When both the area and volume of SGD are known, one can calculate the fresh SGD flux.

Water budget calculations, while relatively simple, are typically imprecise for fresh groundwater discharge estimations because uncertainties associated with values used in the calculations are often of the same magnitude as the discharge being evaluated.

Hydrograph separation techniques: The hydrograph separation technique is based on the assumption that the amount of fresh groundwater entering streams can be obtained via a hydrograph separation and this estimate may be extrapolated to the coastal zone. Two approaches were used to separate the hydrograph for estimating the fresh groundwater flow component. The first method is simply to assign a base flow due to the shape of the hydrograph. The second method of hydrograph separation is the use of geochemical endmember concentrations. Usually, water and geochemical mass balances in a river are shown as follows in equations (3) and (4):

$$D_{\rm T} = D_{\rm S} + D_{\rm G} \tag{3}$$

$$C_{\mathsf{T}}D_{\mathsf{T}} = C_{\mathsf{S}}D_{\mathsf{S}} + C_{\mathsf{G}}D_{\mathsf{G}} \tag{4}$$

where D and C are the discharge rate and geochemical concentrations, respectively, and subscripts T, S and G represent the total, surface water and groundwater components. From those two equations, measured  $D_T$ ,  $C_T$ ,  $C_S$ , and  $C_G$ , we can solve for the two unknown values,  $D_S$  and  $D_G$ .

Theoretical analysis and numerical simulations: Offshore seepage rates were escribed by an exponentially decreasing function, as explained by McBride and Pfannkuch (1975), who investigated the distribution of groundwater seepage rate through lakebeds using numerical models. Bokuniewicz (1992) questioned the use of such an exponentially decreasing function and developed an analytical solution for SGD as follows:

$$q = (Ki/\pi k) \ln[\coth(\pi xk/4l)]$$
(5)

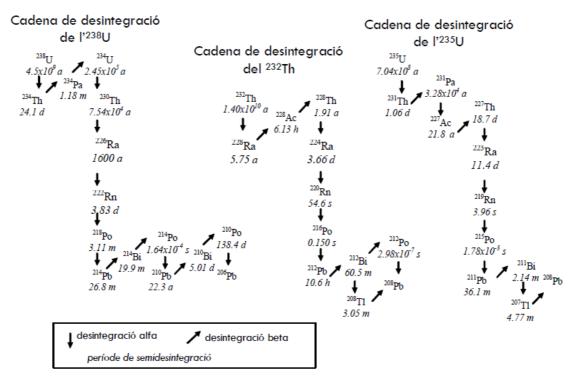
where q is vertical groundwater seepage flux, K is vertical hydraulic conductivity (assumed constant), i is hydraulic gradient, k is the square root of the ratio of the vertical to the horizontal hydraulic conductivity, l is aquifer thickness and x is the distance from the shoreline. The author concluded that a single exponential

function underestimated the analytical solution of SGD both near-shore and far from shore, and overestimated the SGD at intermediate distances. Further details concerning the derivation and use of this equation may be found in Bokuniewicz (1992).

# 1.2.3. QUANTIFICATION WITH Ra AND Rn ISOTOPES

#### Ra isotopes

The four Ra isotopes are found within the natural decay series of U and Th (Figure. 8). These four radium isotopes present half-lives of 3.66 d (<sup>224</sup>Ra), 11.4 d (<sup>223</sup>Ra), 5.75 yr (<sup>228</sup>Ra) and 1600 yr (<sup>226</sup>Ra), making them a powerful quartet for quantifying SGD and associated water exchange processes at different time scales (Bollinger and Moore, 1993; Rama and Moore, 1996; Moore, 1996; Charette *et al.*, 2001).



**Figure. 8:** Radionuclides of the uranium and thorium decay series showing the decay type and half-life of each isotope.

The strategy for using radium isotopes in SGD studies is based on the fact that in freshwater, Ra has a low solubility, although it can be found as dissolved Ra<sup>2+</sup> (Porcelli and Swarzenski, 2003). For these reasons, it is often found attached to the surface of particles and their transport in freshwater is based on the adsorption in colloids and suspended particles (Krest et al., 1999), especially clays and metal hydroxides (Porcelli and Swarzenski, 2003).

In brackish waters, however, Ra behaves as a conservative element because it is desorbed from the particles due to cation exchange processes owing to the higher ionic competition from seawater (Krest et al., 1999, Moore et al., 1995; Webster et al., 1995).

Krest *et al.* (1999) concluded that radium desorption is essentially complete at a salinity of about 5 ppt, so adopting a conservative behaviour once released in sea water.

All these radium isotopes derive from decay of Th parents which are tightly bound to particles whichever the salinity is. Thus, radium is especially useful for SGD studies where subsurface mixing of fresh and salty waters occur. Ideally, radium isotopes should be greatly enriched in groundwater relative to coastal waters (1-2 orders of magnitude) (Moore, 1996) due to the increased ratio between surface of solid aquifer material (containing immobile U and Th) and the amount of water seeping through them. The isotopes accumulate through the processes of dissolution, ion-exchange and alpha particle recoil (Kraemer and Genereux, 1998).

The short-lived isotopes,  $^{223}$ Ra ( $T_{1/2}$  = 11.4 days) and  $^{224}$ Ra ( $T_{1/2}$  = 3.66 days), are continually regenerated from decay of their thorium parents, which are perpetually bound to particle surfaces. On the other hand, the long-lived isotopes,  $^{226}$ Ra ( $T_{1/2}$  = 1600 yrs) and  $^{228}$ Ra ( $T_{1/2}$  = 5.75 yrs), require considerable time for regeneration (Moore, 2003). With the mentioned range of half-lives, Rama and Moore (1996) concluded that this quartet of isotopes can provide powerful constraints on salt marsh hydrology and chemical exchange.

The differences in regeneration rates lead to differences in fluxes of each of these isotopes. The short-lived Ra isotopes can be used to constrain the mixing time of near-shore waters across the shelf. The long-lived ones are useful to evaluate either radium sources or fluxes (Moore, 1999) to the coastal zone under study. These fluxes must be sustained by input from rivers, sea sediments, SGD, or other sources. If we can measure or eliminate all other sources and establish the radium concentration in the groundwater, the radium flux can be directly related to the SGD (Moore, 2003).

# <sup>222</sup>Rn

 $^{222}$ Rn ( $T_{1/2} = 3.83$  days) is a gas produced by the decay of  $^{226}$ Ra.  $^{222}$ Rn is considered a very good tracer to identify areas of groundwater discharge (Burnett and Dulaiova, 2003), mainly due to groundwater is significantly enriched in  $^{222}$ Rn in relation to surface water (3 orders of magnitude or more) and  $^{222}$ Rn is a non-reactive element. Moreover, the fact that the gas  $^{222}$ Rn rapidly exhale into the atmosphere, allows differentiation between groundwater discharges from surface inputs.

The use of continuous <sup>222</sup>Rn to assess the groundwater discharge is a relatively new technique (Burnett and Dulaiova, 2003) that allows to acquire results in a very short time and continuously throughout the study area or period relatively short (as opposed to the methodology based on discrete sampling technique Ra). This allows the characterization of large areas in an acceptable time and integrating the entire sampling area, which makes this technique ideal for the location of areas of groundwater discharge. Thus, this technique has great potential for the location of continental water seeps into the sea, particularly in karst areas where groundwater discharges usually occur in focused ducts of dissolution in carbonate rock.

# 2. STUDY AREA

#### 2. STUDY AREA

# 2.1. HYDRIC SITUATION IN MÁLAGA-GRANADA REGION

Given the difficulty of building new dams and the inconvenience of further increasing pressure on coastal aquifers, many of them already exploited in unsustainable conditions, water policy has had to redirect the one hand, to improve management and implementation of actions to encourage savings, particularly in the agricultural sector, and secondly, to promote the generation of unconventional resources. In this line, in recent years, the reuse of treated effluent for irrigation of golf courses has taken a special boom, and there are currently several ongoing initiatives, which focus on the coastal strip and the Guadalhorce Valley to expand this type of use and extension to agricultural irrigation and urban and industrial uses less stringent.

In terms of desalination, the installation of Marbella is at full performance, whose annual 20hm³ obtained from marine waters are vital to ensure the provision of the Costa Sol, and also of the Atabal, allowed to produce up 60hm³/year water resources by treating brackish water, and whose role will be essential for the supply of the capital while the resolution of the problem of salt contamination in Guadalhorce reservoir and alluvial aquifer isn't solved. To these plants, the second floor of the western commonwealth will be added in a relatively short time, to be located in Mijas, close to the city of Fuengirola, which is projected with an initial capacity, expandable, similar to that of Marbella.

Looking to overwhelming perspectives for growth in water demand (according to statements drawn up for the Mediterranean area, in 2000 the net resources available hm³ stood at 525 hm³, while the demand forecast for 2018 amounted to 675 hm³), with the forecast (which match the various climate change scenarios) that in the next 20 years, the reduction of inputs will be of 10%, increasing the hydrological irregularity peninsular, and accentuating the imbalances in Mediterranean Basins, the solution in a medium - long term to increase water availability in the province of Málaga needs to look for new surface infrastructure regulation, complemented by desalination of sea water to supply the population near the coast, and to maximize (mostly in the same geographical area) reuse of treated wastewater for uses compatible with its quality, especially for agricultural irrigation, urban and golf courses. Only this way can guarantee the future needs without causing severe impacts, or even critical, on the water environment, impacts that otherwise would be incompatible with the objectives of the Water Framework Directive.

This strategy will also entail additional benefits, including the recovery of aquifers nowadays exploited in an abusive way, and its rehabilitation as strategic reserves. But perhaps the positive effect of greater significance for society of Malaga would be their contribution to a more balanced territorial development. The use of unconventional resources in the coastal strip and surrounding areas would free up the reservoirs of some of the demands assigned to them, which would create surpluses that could be utilized in the inland municipalities whose growth is now mortgaged by the high consumption of the littoral.

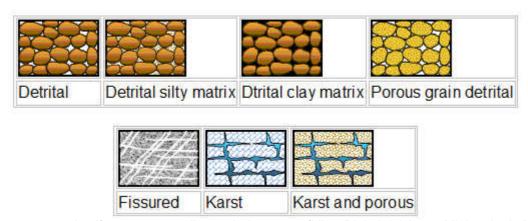
#### 2.2. THE AQUIFER

# 2.2.1. DESCRIPTION AND TYPES

An aquifer is that geological formation, consisting of one or more layers of rocks (gravel, sand, limestone, etc.) that can store and transmit water through them in significant quantities, so that it can be extracted by headworks. The aquifers have very different surface dimensions and thickness.

Aquifers can be classified according to the type of materials they contain or as hydraulic and structural circumstances. In the first case aquifers generally could be:

- Porous aquifers when the permeability is due to intergranular porosity (e.g. gravel, sand). In general all detrital material with sand grain size minimum.
- Karst and fissured aquifers whose permeability is due to cracks and fissures of both origin mechanical and dissolution. These include limestone, dolomite, granite, basalt, etc.., being the first two the major types.

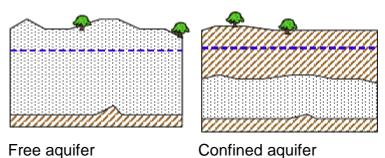


**Figure. 9:** Aquifer types according to their texture. (Libro Digital del Agua. Ministerio de Medio Ambiente y Medio Rural y Marino. Gobierno de España).

Depending on hydraulic and structural circumstances, aquifers can react in three different ways (Figure. 10 and 11):

- Free aquifer: are those in which the water level is below the permeable formation. The water flow is the drainage from the pores.
- Confined aquifer: are those covered by an impermeable confining layer. The water level in captive aquifers is above the aquifer formation. The water flow is due to the expansion of water and decompression of vertical permeable structure, when depression occurs in the aquifer. Also they are called captive aquifers.
- Semiconfined aquifers: can be considered a special case of captive aquifers, in which wall, ceiling, or both are not completely waterproof, but allow vertical movement of water. Actually semiconfined aquifer can be physical system composed of well-fed upper aquifer, semi-permeable package and lower semiconfined aquifer. The difference in levels

between the upper and lower aquifer leads to a vertical transfer of water that feeds the lower aquifer.



**Figure. 10:** Aquifer types depending on their structure and functioning.

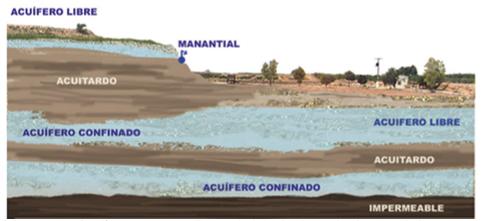


Figure. 11: Aquifer types according to their hydrodynamic characteristics

# 2.2.2. THE AQUIFER OF THE HYDROGEOLOGICAL SUBUNIT OF "LAS ALBERQUILLAS".

In the "Proyecto de Plan Hidrológico de la Demarcación Hidrográfica de las Cuencas Mediterráneas Andaluzas" there are summary sheets of the different water bodies. There, is also explained that in the Hydrographic Mediterranean District 67 acuifers have been identificated (Figure. 12), 7 of which are in low permeable land, but where there are significant deposits for human consumption. Those 67 acuifers are classified in five systems (Figure. 13).

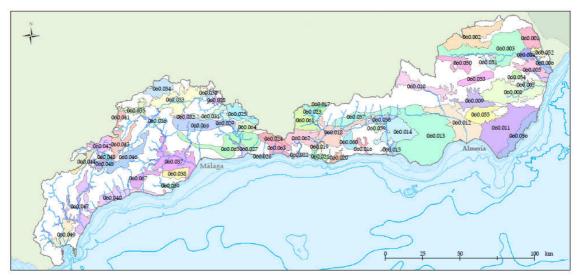
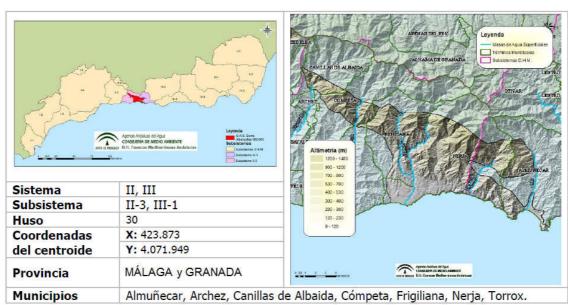


Figure. 12: The 67 acuifers in the Hydrographic Mediterranean District



Figure. 13: Location of the Hydrographic Mediterranean District and the five systems.

The name of the subsurface water body is "Sierra Alberquillas" and it's the number 060.063. It has an area of 11.714 ha. and an outcrop of 77.3 km<sup>2</sup>. The acuifer is non confined and belongs to the system II and III and the subsystems II-3 and III-1 (Figure. 14).



**Figure. 14:** Location of the acuifer "Sierra de Alberquillas". Source: Junta de Andalucía. Consergería de Medio Ambiente. Agencia Andaluza del Agua.

## There are fourteen areas protected to supply:

Protected a	reas to supply				
Name	Coordinates				
Nume	X UTM	Y UTM			
Adelfa	413.376	4.077.090			
Barranco Pérez	413.702	4.077.110			
El Peñoncillo	416.062	4.074.813			
Cueva de los Bojes	421.517	4.070.492			
Canal San Isidro	421.606	4.070.124			
La Cantera	421.553	4.070.091			
Los Bolicheros	421.680	4.069.677			
Castillo Alto	421.443	4.067.698			
Maro	425.198	4.068.680			
Corta 3º de la Fábrica	421.169	4.071.486			
Cantarriján I	430.392	4.067.879			
Cantarriján II	430.395	4.067.657			
Cantarriján III	430.399	4.067.658			
Cantarriján IV	430.333	4.068.020			

## And seven networks of control:

Código	Nombre	Coor	denadas	Programa de control	
Courgo	Nonible	X UTM	Y UTM	Programa de control	
C.06.24.003-B	Cantariján	430.375	4.067.750	Químico	
P.06.24.005-B	Cantarriján. Almuñecar	430.750	4.066.375	Químico	
C.06.24.002-B	Río Chillar	421.675	4.070.225	Químico	
P.06.24.001-S	Sond.Tejeda- Almijara IN-06	429.559	4.070.820	Cuantitativo	
P.06.24.002-S	Cueva de Nerja	424.451	4.069.106	Cuantitativo	
P.06.24.004-B	Río Chillar	421.636	4.070.425	Cuantitativo	
P.06.24.005-B	Cantarrijan	430.727	4.066.793	Cuantitativo	

In this study is analised the quantitative, chemical and global state and it's concluded that is BAD because of (1) Over-explotation of aquifers, saltwater intrusion and other processes of salinization and (2) Urban pollution. The solutions they found are (1) Constitution of users community and develop a business plan, (2) Implementation of connection and distribution infrastructures and (3) Promotion of reusing resources for agricultural irrigation and (4) Improvements in the sewerage system.

The environmental objective is to rise the best state of the aquifer in 2021.

In a work from Malaga's University and the Instituto Geológico y Minero de España (IGME) they explain that in Sierra Almijara-Alberquillas aquifer (Figure. 15) is taken 15hm³/year for water supply in the Malaga's region (Figure. 16). Although this acuifer is bigger than Sierra Alberquillas, a global view could be taken.

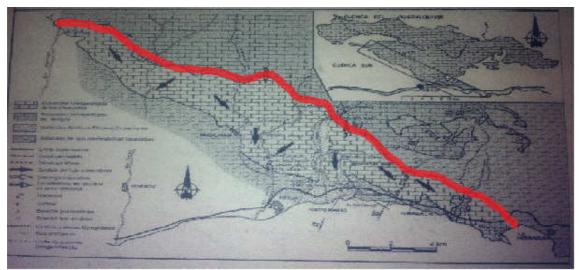


Figure. 15: Sierra Almijara (north) Alberquillas (south) aquifer separation with water flow arrows. (Modified from Carrasco, F. et al., 1988)

Acuíferos de la provincia de Málaga						
Nombre del acuífero (nº de masa de agua subterránea donde se incluye)	Superficie km²	Recursos hm³/año	Bombeo hm³/año	Usos/Observaciones		
Sierra Almijara-Alberquillas (060.024) (060.063) *	142	50	15	Compartido con Granada. Abastecimiento a Torrox, Nerja, Frigiliana, Cómpeta, C. Albaida y otros de Granada. Riegos. Indicios de intrusión.		

**Figure. 16:** Hydric resource and degree of explotation. (Atlas Hidrogeológico de Málaga. Univ. de Málaga and IGME).

# 3. MATERIAL AND METHODS

#### 3. MATERIAL AND METHODS

#### 3.1. SAMPLING METHODOLOGY

There have been sampled a total of 48 stations in the sea for the analysis of Ra isotopes and distributed between Maro and Almuñécar and 12 stations in wells, piezometers and springs in the area (Figure 17). It has also been made specific continuously sampling in Rn, drawing parallels at various distances from the coastline (along the isobaths of 5 m, 20 m, 30 m and 50 m from the coast). The field work was conducted in four sampling campaigns: 14-15 September 2006, 19-20 September 2006, 11-13 November 2009 fully tailored to Rn, and 21-24 September 2010 . The study area for the determination of Rn are shown in Figure 17.

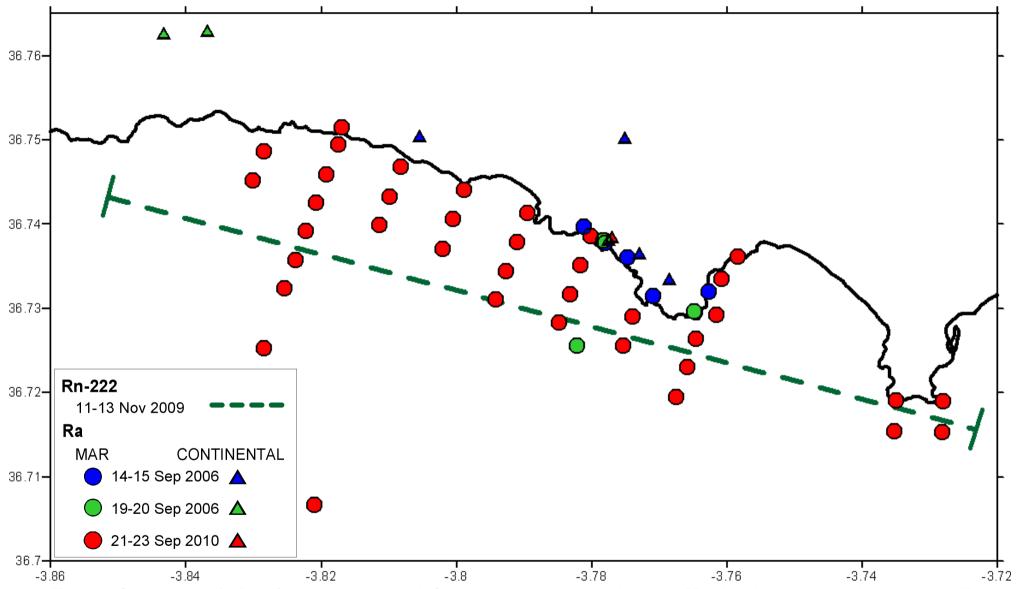
#### 3.1.1. WATER SAMPLES

Radium isotope activities are typically present at such low levels in natural waters, especially in seawater, that their measurement requires preconcentration from large samples. This can be accomplished by passing large volumes (20 to 100 L) of water through a cartridge loaded with MnO<sub>2</sub>-impregnated acrylic fiber, which quantitatively extracts radium isotopes by adsorbing them onto the MnO<sub>2</sub> particles (Moore, 1976).

The MnO<sub>2</sub>-impregnated acrylic fiber (Mn-Fiber) is prepared by immersing the raw acrylic fiber for about 15 minutes in saturated KMnO<sub>4</sub> solution (64 g·L<sup>-1</sup>) heated to 75°C. The KMnO<sub>4</sub> oxidizes specific sites on the acrylic molecule and deposits MnO<sub>2</sub> at these sites. This process produces Mn-fiber having submicrometer sized particles of MnO<sub>2</sub> chemically bonded to the fiber. The process of Mn-fiber preparation is carried out under continuous stirring and the temperature is strictly controlled. Keeping a good mixing is needed to maintain the KMnO<sub>4</sub> permanently dissolved so that a homogeneous impregnation of the fiber is achieved. Temperature control is also a key issue. At temperatures lower than 75°C, more time is required; for example, several days are needed at temperatures of 30-35°C (Michel et al., 1981). The exothermic reaction proceeds very rapidly at temperatures over 80°C, and the Mn-fiber can be destroyed due to strong oxidation.

When the fiber turns black, it is quickly removed from the bath and rinsed thoroughly (Moore, 1976). Radium-free water, prepared by passing deionized water through previously prepared Mn fiber is used along all the procedure. After a final rinse in radium-free water, the fiber is hand-squeezed and stored in plastic bags until use.

In the field, approximately 150 cm<sup>3</sup> (~50 g wet weight or ~25 g dry weight) of Mn-fiber is loosely introduced into a cylindrical PVC column. Loosing the fiber is important to maximize the active surface for radium adsorption.



**Figure 17:** Sampling points for Ra análisis during campaings in September 2006 and 2010, and transect of Rn along the coast done in November 2009. The station codes correspond to samples of sea water and the control points of ground water (springs and boreholes) in the discharge area.

#### 3.2. ANALYSIS PROCEEDING

#### 3.2.1. Ra

In the quantification of the isotopes of Ra there are two different procedures, one for determining the activities of short-lived isotopes (<sup>223</sup>Ra and <sup>224</sup>Ra) and one long-lived isotopes (<sup>226</sup>Ra and <sup>228</sup>Ra).

# 3.2.1.1. Short-lived isotopes

Each Mn fiber sample is cleaned with distilled water, free of Ra, to remove particles that may interfere with the measure. Then, the Mn fibers are partially dried in order to get ratio fiber/water optimal for measuring Ra (0.3 to 1  $gH_2O/gfiber$ , Sun and Torgersen, 1998).

Once conditioned, the fiber are placed in the computer RaDeCC (Radium Delayed Coincidence Counter, Figure. 18) to measure <sup>223</sup>Ra and <sup>224</sup>Ra isotopes according to the method described by Moore and Arnold (1996) and Garcia-Solsona et al. (2008). The same sample is measured three times with RaDeCC over 1 month: (1) immediately after sample collection to minimize the radioactive decay of <sup>224</sup>Ra, (2) one week after the first measure, to quantify <sup>223</sup>Ra, and (3) after a month of sample collection to allow the initial excess of <sup>224</sup>Ra would balance with <sup>228</sup>Th adsorbed to the fiber and determine the basic <sup>228</sup>Th.

### 3.2.1.2. Long-lived isotopes

Having analyzed short-lived isotopes, the Mn fibers are incinerated in a furnace at 820°C for 16 hours (Charette et al., 2001). Fiber incinerated, once crushed and homogenized, is transferred into polyethylene cylindrical minivials 6 cm3 (Zinsser ©) with different graduate volumes. The vials are sealed and stored for three weeks before the quantification, to achieve secular equilibrium between <sup>226</sup>Ra and its short-lived daugthers. The minivials are measured by gamma spectrometry (Figure. 19) for 80,000 to 350,000 seconds depending on the activity of the samples. <sup>228</sup>Ra activity is calculated from radioactive decay of <sup>228</sup>Ac through the emission line of 911 keV and that of <sup>226</sup>Ra is determined by the activity of <sup>214</sup>Pb photopeak at 352 keV.

### 3.2.2. Rn

Quantification of  $^{222}$ Rn in water samples contained in vials of 250 mL was performed with the RAD-7 equipment and the accessory RAD-H<sub>2</sub>O to measure Rn in water with high precision (Durridge Co. , Inc.). The portability of this equipment allowed the measurement of  $^{222}$ Rn both field and laboratory, minimizing the time decay of  $^{222}$ Rn.

#### 3.3. DETECTION SYSTEMS

#### 3.3.1. RaDeCC

The RaDeCC (Radium Delayed Coincidence Counter) is an equipment of alpha solid scintillation detection based on a closed system of helium gas flow through Mn-fiber (Figure. 18). The gas drag isotopes <sup>219</sup>Rn and <sup>220</sup>Rn derived from the decay of <sup>223</sup>Ra and <sup>224</sup>Ra of the fiber to the scintillation cell where alpha particles produced by the decay of in Rn and Po are measured. The RaDeCC uses the difference between the constants of decay of Po isotopes coming from the decay of <sup>219</sup>Rn and <sup>220</sup>Rn to differentiate the activities of <sup>223</sup>Ra and <sup>224</sup>Ra (Moore and Arnold, 1996).



Figure. 18: RaDeCC equipment used for the measurement of <sup>223</sup>Ra and <sup>224</sup>Ra.

#### 3.3.2. GAMMA SPECTROMETRY

The gamma spectrometry system used is a well germanium detector of high purity (model GMX-20190 CANBERRA brand), coated with a passive shield of lead and copper and connected to a CANBERRA ADC (model 8701) of 8192 channels of resolution (Figure. 19). This system allows the distinction of different gamma emissions of radionuclides (from 3 keV to 10 MeV) and allows the measurement of environmental samples with low activity due to its high efficiency.

To carry out the analysis of the spectra using the program Genie 2000, that allows full analysis of a range of gamma emitters, depending on the values of measurement, calibration and other information of interest (measurement time, background, detector ...)



**Figure 19:** Interior of Ge well detector (gamma spectrometry) used for the measurement of <sup>226</sup>Ra and <sup>228</sup>Ra with a minivial at place.

#### 3.3.3. RAD7

The RAD7 is a portable monitor of <sup>222</sup>Rn and <sup>220</sup>Rn in air marketed by Durridge Co. RAD7 is based on a silicon semiconductor detector with a high electric field to attract the Po isotopes (radioactive daughters of <sup>222</sup>Rn) which is positively charged and alpha emitters (+ <sup>218</sup>Po, <sup>214</sup>Po +), which are then counted to infer the concentration of <sup>222</sup>Rn in air. In addition, the RAD7 allows energetically differentiation of the isotopes of Po as a function of their alpha energy.

Given that the detector is an RAD7 in air, for measurements of <sup>222</sup>Rn in water, system requires the balancer air-water RAD-Aqua. The method is based on spreading the flow of water to be sampled by passing it through the RAD-Aqua (which incorporates a diffuser), with the aim of facilitating the <sup>222</sup>Rn air and water reach equilibrium quickly. The air of the balancer (containing <sup>222</sup>Rn in equilibrium with <sup>222</sup>Rn in air), flows through the RAD7 to determine the concentration of <sup>222</sup>Rn in air, and from this value derive to the concentration of <sup>222</sup>Rn in water.



**Figure. 20:** Air-water balancing RAD-Aqua connected to three parallel RAD7 to determine the concentration of <sup>222</sup>Rn in water.

# 4. RESULTS AND DISCUSSION

#### 4. RESULTS AND DISCUSSION

#### 4.1. Rn

In order to identify the main area of groundwater discharge between Maro and Punta de la Mona, continuously <sup>222</sup>Rn concentration was measured in 4 parallel transects to the coastline and following the depth contours of 5m, 20m, 30m and 50m (Figure. 21a).

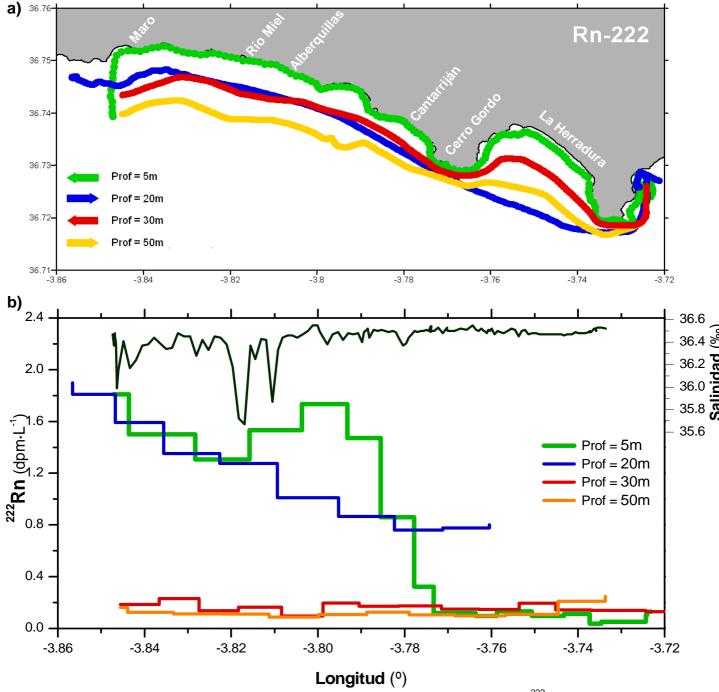
<sup>222</sup>Rn activities measured in the sampling area, with maximum of 2 dpm·L<sup>-1</sup>, are very low compared with areas with similar characteristics (e.g. 4-12 dpm·L<sup>-1</sup> in Garraf, Barcelona, in months with low discharge submarine). Only in the transect closest to the coast line (green line in Figure. 21a) were measured <sup>222</sup>Rn concentrations statistically higher than 0 Bq·m<sup>-3</sup>. The values of the transect of 20 m deep (blue), which appear as quantifiable activities, are the product of equilibrium time required by the computer to eliminate the influence of the measurements of <sup>222</sup>Rn, relatively high, the transect closest to the coast (immediately prior to continuously of 20m in depth).

The Rn increases observed along the transect of 5 m depth, are mainly between Maro and Cerro Gordo, coinciding with major decreases of salinity along the transect (up to a salinity of 35.7 ‰). This would suggest that groundwater discharge should occur mainly in the western part of the study area, between Maro and Cerro Gordo. However, is important to note that major decreases in salinity coincide with surface discharges of Miel River, the source of the Alberquillas and the spring of Maro. Thus, the coastal waters where there are higher concentrations of <sup>222</sup>Rn, would come from the discharge of fresh surface water, which at the same time are due to the aquifer groundwater discharge. On the other hand, it is noted that when measuring surface salinity along the other transects no noteworthy variations in salinity were showed (with constant values between 36.35 and 36.55), nor variations of <sup>222</sup>Rn, which indicates that continental water output into the sea was not detected. However, the measuring depth (30-50 m) could be a limitation when analysing <sup>222</sup>Rn in surface water.

The low activities of <sup>222</sup>Rn measured in the study area, with slightly higher concentrations in areas influenced of surface freshwater inputs show that the contribution of <sup>222</sup>Rn through groundwater discharges is small. This suggests that groundwater discharge in the area of Maro-Almuñécar is volumetrically insignificant.

# 4.2. Ra

The concentrations of Ra isotopes (<sup>223</sup>Ra, <sup>224</sup>Ra, <sup>226</sup>Ra and <sup>228</sup>Ra) of the samples analyzed are presented in Tables 4 and 5, together with the data of salinity, temperature and time of sample collection. <sup>224</sup>Ra activities of the campaign in September 2010 are shown in Figure. 22.



**Figure. 21:** a) Transects described for the determination of the concentration of <sup>222</sup>Rn during the November 2009 campaign. The different colors indicate isobaths along transects (5m, 20m, 30m and 50m) and the arrows of the legend the direction in which transects were conducted. b) Activities of <sup>222</sup>Rn measured along the transects, in different colors representing the different transects. It is also represented the salinity along the transect closest to the coast, following the 5m depth contour.

**Table 4:** Activity of Ra isotopes (224, 223, 226, 228Ra) of all stations sampled in September 2006 campaigns, together with the salinity, temperature and time of sampling.

<b>N</b> 4		Cordenadas Latitud (N) Longitud (W)		Temp	Sal	<sup>224</sup> Ra	<sup>223</sup> Ra	<sup>226</sup> Ra	<sup>228</sup> Ra
Muestra	Fecha y Hora			°C	<b>‰</b>	$(dpm \cdot 100L^{-1})$			
14-15 Septiembre 2006									
Mar									
CerroGordoMar	14/9/2006 15:15	36.7315	3.7710	22.0	37.0	$5.1~\pm~0.6$	$1.2\ \pm\ 0.2$	N.A.	<mda< td=""></mda<>
PlVelilla	14/9/2006 12:40	36.7355	3.6685	22.6	36.8	$18.7\ \pm\ 1.2$	$1.4\ \pm\ 0.2$	$25.4\ \pm\ 1.0$	<mda< td=""></mda<>
CuevaCantRij	14/9/2006 18:00	36.7378	3.7781	25.7	37.0	$7.0~\pm~0.7$	$1.5~\pm~0.2$	<mda< td=""><td><mda< td=""></mda<></td></mda<>	<mda< td=""></mda<>
PlayaCantRij	14/9/2006 19:15	36.7361	3.7748	23.9	37.1	$12.1\ \pm\ 0.9$	$1.1\ \pm\ 0.2$	$16.9~\pm~0.3$	<mda< td=""></mda<>
CañueloEste	15/9/2006 10:30	36.7397	3.7812	17.6	37.3	$6.4~\pm~0.6$	$0.3 \pm 0.1$	$30.6 \pm 0.4$	<mda< td=""></mda<>
Herradura	15/9/2006 15:15	36.7320	3.7627	17.4	37.5	$5.3~\pm~0.5$	$0.7 \pm 0.1$	$5.7~\pm~0.2$	<mda< td=""></mda<>
Continental									
CT_PozoSeverino	14/9/2006 18:30	36.7364	3.7730	22.4	2.5	$86.8 \pm 6.0$	$1.7\ \pm\ 0.4$	$355.1 \pm 1.3$	$99.7 \pm 1.6$
CT-10	14/9/2006 14:25	36.7333	3.7686	24.0	2.2	$125.9 \pm 9.4$	$102.1 \pm 5.2$	$818.8\ \pm\ 2.5$	$125.8 \pm 2.3$
CT-2	15/9/2006 10:00	36.7502	3.7751	22.8	0.6	$102.4 \pm 7.7$	$9.0  \pm  1.3$	$90.2 \pm 1.1$	$108.8 \pm 3.0$
ManAlberquillas	15/9/2006 8:40	36.7503	3.8055	22.5	0.3	$58.5\ \pm\ 2.9$	$4.8~\pm~0.4$	N.A.	N.A.
19-20 Septiembre 2006									
Mar									
CGordoSifon	19/9/2006 13:06	36.7297	3.7649	16.8	37.0	$2.8~\pm~0.4$	$0.3 \pm 0.1$	$12.4~\pm~0.2$	$3.6 \pm 0.3$
CuevaCantRij	19/9/2006 13:16	36.7381	3.7783	16.8	37.0	$6.0~\pm~0.5$	$0.3 \pm 0.2$	$7.7~\pm~0.2$	N.A.
MarAbierto	19/9/2006 13:26	36.7257	3.7822	17.6	37.0	$2.7~\pm~0.3$	$0.7 \pm 0.2$	$12.3 \pm 0.3$	N.A.
Continental									
CV-1	20/9/2006 12:55	36.7625	3.8434	21.2	0.4	$18.2\ \pm\ 1.3$	$1.6 \pm 0.2$	$35.0~\pm~0.3$	$14.2~\pm~0.6$
ManMaro	20/9/2006 10:14	36.7628	3.8369	19.3	0.4	$57.0\ \pm\ 2.2$	$7.3\ \pm\ 1.0$	$1781.3 \pm 3.1$	$43.3 \pm 1.1$

N.A. No analised

MDA. Minimum detectable activity

For the September 2006 campaign, the concentrations of  $^{224}$ Ra in seawater measures range from 18.7 ± 1.2 dpm·100L<sup>-1</sup> in Velilla Beach and 2.7 ± 0.3 dpm·100L<sup>-1</sup> in the sample of open sea. It suggests that the measure of Velilla Beach came after a stormy day in which there were contributions from sea water from surface streams. For  $^{223}$ Ra the maximum concentration in the sea is 1.5 ± 0.2 dpm·100L<sup>-1</sup> in the cave of Cantarriján and 0.3 ± 0.2 dpm·100L<sup>-1</sup> at several stations. The  $^{226}$ Ra concentration varied between 30.6 ± 0.4 dpm·100L<sup>-1</sup> on the beach of Cañuelo and 12.3 ± 0.3 dpm·100L<sup>-1</sup> in the open sea station.

**Table 5:** <sup>224</sup>Ra activity of samples taken in the campaign in September 2010, together with the salinity, temperature and time of sampling.

		Cord	enadas	Temp	Sal	<sup>224</sup> Ra	
Muestra	Fecha y Hora	Latitud (N)	Longitud (W)	°C	‰	(dpm·100L <sup>-1</sup> )	
21-23 Septiembre 2010							
Mar							
MLG03	21/9/2010 8:15	36.7515	3.8170	21.86	36.49	$2.1 \pm 0.2$	
MLG09	23/9/2010 8:10	36.7362	3.7585	22.05	36.44	$3.1 \pm 0.3$	
MLG13	21/9/2010 8:35	36.7495	3.8176	21.69	36.25	$5.6 \pm 0.4$	
MLG14	22/9/2010 15:40	36.7468	3.8083	22.87	36.37	$1.6 \pm 0.2$	
MLG15	22/9/2010 17:12	36.7441	3.7989	22.94	36.50	$1.3 \pm 0.2$	
MLG16	22/9/2010 9:45	36.7414	3.7896	22.26	36.36	$2.0 \pm 0.2$	
MLG17	22/9/2010 9:02	36.7386	3.7802	21.80	36.36	$5.1 \pm 0.4$	
MLG17prof	23/9/2010 9:25	36.7386	3.7802	22.88	36.40	$2.3 \pm 0.3$	
MLG19	23/9/2010 10:24	36.7335	3.7609	22.11	36.41	$2.0 \pm 0.2$	
MLG22	22/9/2010 16:20	36.7487	3.8286	23.35	36.35	$1.5 \pm 0.2$	
MLG23	21/9/2010 8:50	36.7460	3.8193	21.95	36.49	$0.8 \pm 0.1$	
MLG24	22/9/2010 15:50	36.7433	3.8099	22.77	36.36	$1.4 \pm 0.2$	
MLG25	22/9/2010 17:02	36.7406	3.8006	23.23	36.35	$1.1 \pm 0.1$	
MLG26	22/9/2010 11:09	36.7379	3.7911	22.28	36.37	2.2 ± 0.2	
MLG27	22/9/2010 9:17	36.7352	3.7817	22.11	36.39	$1.4 \pm 0.2$	
MLG29	23/9/2010 9:50	36.7293	3.7616	22.07	36.42	$1.7 \pm 0.2$	
MLG32	22/9/2010 16:25	36.7453	3.8302	23.94	36.31	1.1 ± 0.1	
MLG33	21/9/2010 9:10	36.7426	3.8208	22.02	36.49	$1.2 \pm 0.2$	
MLG34	22/9/2010 16:05	36.7399	3.8114	23.21	36.35	$0.8 \pm 0.1$	
MLG35	22/9/2010 16:47	36.7371	3.8020	23.20	36.34	$0.8 \pm 0.1$	
MLG36	22/9/2010 0:00	36.7345	3.7927	22.50	36.37	$0.6 \pm 0.1$ $1.5 \pm 0.2$	
MLG37	22/9/2010 0:00	36.7318	3.7833	22.27	36.37	$1.2 \pm 0.2$ $1.2 \pm 0.2$	
MLG37 MLG38	22/9/2010 9:23	36.7291	3.7740	22.25	36.36	$2.3 \pm 0.2$	
MLG38prof	23/9/2010 10:05	36.7291	3.7740	20.43	36.48	$1.9 \pm 0.2$	
MLG38ptot MLG39	21/9/2010 14:34	36.7264	3.7647	22.38	36.45	$1.9 \pm 0.2$ $2.0 \pm 0.2$	
MLG43	21/9/2010 14:34	36.7392	3.8223	22.13	36.49	$0.8 \pm 0.1$	
						$0.8 \pm 0.1$ $0.9 \pm 0.1$	
MLG46	22/9/2010 11:32	36.7311	3.7943	22.27	36.37		
MLG47	22/9/2010 8:34	36.7284	3.7849	22.26	36.35	$1.4 \pm 0.2$	
MLG48	22/9/2010 8:20	36.7256	3.7754	22.23	36.37	$1.2 \pm 0.2$	
MLG49	21/9/2010 14:56	36.7230	3.7660	22.30	36.45	$1.5 \pm 0.2$	
MLG53	21/9/2010 9:30	36.7357	3.8239	22.09	36.49	$1.0 \pm 0.2$	
MLG59	21/9/2010 15:07	36.7195	3.7676	22.04	36.44	$1.7 \pm 0.2$	
MLG63	21/9/2010 9:45	36.7324	3.8255	21.93	36.45	$0.5 \pm 0.1$	
MLG83	21/9/2010 11:50	36.7253	3.8286	22.52	36.42	$0.8 \pm 0.1$	
MLGOPEN	21/9/2010 11:30	36.7067	3.8211	22.67	36.47	$0.6 \pm 0.1$	
MLG_MONA1	23/9/2010 8:30	36.7191	3.7351	22.62	36.44	$1.6 \pm 0.2$	
MLG_MONA2	23/9/2010 7:55	36.7190	3.7281	22.75	36.42	$1.3 \pm 0.2$	
MLG_MONA3	23/9/2010 8:21	36.7155	3.7353	22.78	36.47	$1.4 \pm 0.2$	
MLG_MONA4	23/9/2010 8:10	36.7153	3.7282	22.50	36.44	$1.9 \pm 0.2$	
ontinental							
CT_PozoSeverino	21/9/2010 17:30	36.7383	3.7771	21.73	1.63	$65.8 \pm 2.8$	
MLG_Pz_CT1	21/9/2010 20:00	36.7380	3.7776	22.10	14.90	$224.5 \pm 18.9$	
MLG_Pz_CT2	22/9/2010 9:00	36.7380	3.7776	22.50	6.62	$78.5\ \pm\ 5.5$	
MLG_Pz_CT3	22/9/2010 10:00	36.7380	3.7776	23.87	12.19	$129.2~\pm~8.3$	
MLG_Pz_CT4	22/9/2010 0:54	36.7380	3.7776	24.80	31.07	$550.5 \pm 43.2$	
MLG_Pz_CT5	22/9/2010 13:45	36.7380	3.7776	25.57	24.21	$397.4 \pm 16.0$	

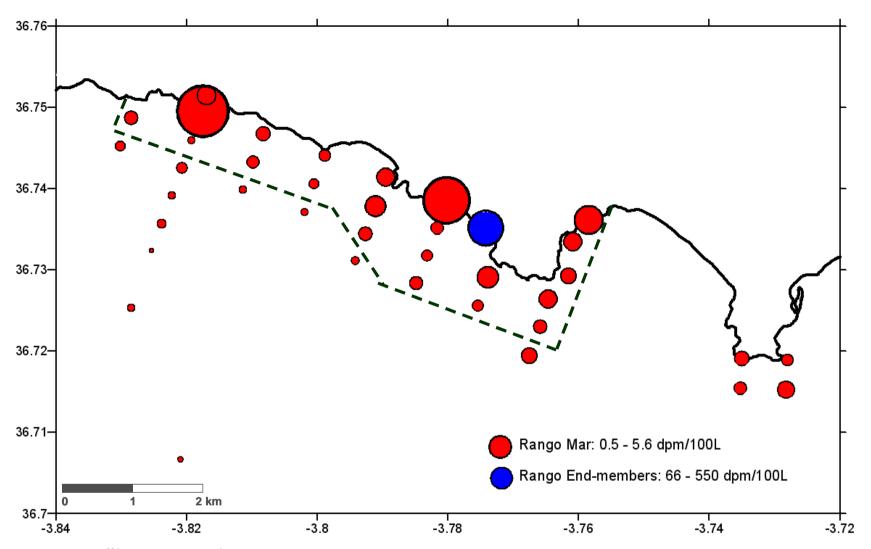
Regarding the concentrations of  $^{224}$ Ra in the sea of September 2010 campaign, the concentration of  $^{224}$ Ra varies between 5.6  $\pm$  0.4 dpm·100L<sup>-1</sup> in MLG13 station, in front of the mouth of Rio Miel, and 0.6  $\pm$  0.1 dpm·100L<sup>-1</sup> in MLGOPEN station offshore. The average concentrations in the ocean is 1.7  $\pm$  1.2 dpm·100L<sup>-1</sup>. As in the case of  $^{222}$ Rn,  $^{224}$ Ra highest value corresponds to the mouth of Rio Miel, suggesting that these high values of Ra are linked to river discharge.  $^{223}$ Ra concentrations in samples of sea is less than the detection limits of the technique (0.3 dpm·100L<sup>-1</sup>).

There is a significant difference in the results of measurements of salinity and <sup>224</sup>Ra activities carried out in September 2006 and September 2010. In general, samples from September 2006 are more active than 2010 because the samples are taken directly from the beach where the concentrations are higher due to the possible direct influence sediment. There is also a difference between open water samples taken in both campaigns. The activity in open sea in September 2006 is 2.7 ± 0.3 dpm 100L<sup>-1</sup> with a salinity of 37.0 ‰ while in September 2010 the activity of the sample MLG47 (which coincides geographically with the above) is  $1.4 \pm 0.2$  dpm  $100L^{-1}$  with a salinity of 36.35 %. Is also noteworthy the low salinity and <sup>224</sup>Ra activity measured in the sample of open water in September 2010 (MLG-OPEN: 0.6 ± 0.1 dpm-100L<sup>-1</sup> with a salinity of 36.50 ‰) compared with the measured activities in the Western Mediterranean (e.g.  $1.7 \pm 0.5$  dpm  $100L^{-1}$  in the waters of Menorca with a salinity of 38.1 % (Garcia-Solsona et al., 2010a). This difference is likely due to the coast of Malaga is influenced by the mixing of waters from the Atlantic Ocean (salinity 36.2 %) with Mediterranean Sea (38.2 %).

<sup>224</sup>Ra activities in boreholes, springs and piezometers at different campaigns, range from 18.2 ± 0.3 dpm·100L<sup>-1</sup> (sounding of the Cave of Nerja, salinity 0.4 ‰) and 550 ± 40 dpm·100L<sup>-1</sup> (piezometer made in Cantarriján beach, salinity 31.1 ‰). Figure. 23 shows and compares the concentrations of <sup>224</sup>Ra in water from the piezometers, springs and boreholes and the concentrations in samples of seawater. <sup>224</sup>Ra concentration of probes and piezometers is clearly influenced by water salinity, as the Ra desorbs from the particles due to cation exchange processes in seawater (Krest et al., 1999, Moore et al., 1995, Webster et al., 1995).

There are different methods for calculating the groundwater discharge into the sea based on a mass balance of Ra isotopes (Moore, 1996, Hwang et al., 2005; Moore, 2003; Krest and Harvey, 2003). The methods, based on different boundary conditions require, in general, the calculation of flow balance Ra ( $^{224}$ Ra, in this study) from the mainland to the sea through groundwater discharges ( $^{224}$ Ra $_{xs}$ ) and estimate of Ra in the groundwater aquifer ( $^{224}$ Ra $_{SGD}$ ) that discharges to the sea ( $''end\mbox{-}member''$ ) so that the discharge is determined by the equation (6):

$$SGD[m^{3} \cdot y^{-1}] = \frac{{}^{224}Ra_{xs}[Bq \cdot y^{-1}]}{{}^{224}Ra_{gw}[Bq \cdot m^{-3}]}$$
(6)



**Figure. 22:** Activities of <sup>224</sup>Ra (dpm · 100L<sup>-1</sup>) in sea and inland stations (piezometers and boreholes) sampled during the campaign in September 2010. The dashed line indicates the area used for the calculation of groundwater discharge. The study area has been delimited on the basis of bathymetry and Ra and <sup>222</sup>Rn concentrations observed.

The calculation of  $^{224}\text{Ra}_{xs}$  is based on determining the contribution of  $^{224}\text{Ra}$  of potential sources of  $^{224}\text{Ra}$  to the sea (e.g. rivers and sediment) and attributing to the SGD the excess of  $^{224}\text{Ra}$  that can not be provided by them, taking into account the baseline of  $^{224}\text{Ra}$  open sea water. Considering that all contributions of  $^{224}\text{Ra}$  come exclusively from groundwater discharge,  $^{224}\text{Ra}_{xs}$  would be determined by the difference between the average activity of  $^{224}\text{Ra}$  in the study area and the activity of  $^{224}\text{Ra}$  in open sea. In the September 2010 sampling, the mean activity of  $^{224}\text{Ra}$  (weighted according to depth) in the study area (dashed line in Figure. 22) is  $1.5 \pm 0.8$  dpm· $100L^{-1}$ , while the activity  $^{224}\text{Ra}$  in the sample of open ocean is  $0.6 \pm 0.1$  dpm· $100L^{-1}$ , which implies a  $^{224}\text{Ra}_{xs}$  activity of  $0.9 \pm 0.8$  dpm· $100L^{-1}$ , assuming a  $1\sigma$  uncertainty.

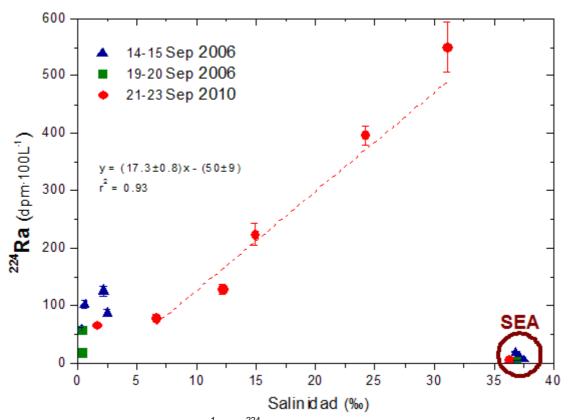
Given small excess of <sup>224</sup>Ra on the coast (close to 0, statistically), and considering that the entire <sup>224</sup>Ra proceeds of SGD, the results indicate that the discharge is low or not detectable by the technique of Ra isotopes. This conclusion would be supported by another tracer like <sup>222</sup>Rn, which is enriched by a different geochemical processes, and reveals qualitatively that the discharge of groundwater in the area is minimal.

However, if we consider this difference ( $^{224}$ Ra<sub>xs</sub>) as statistically significant, we could estimate the maximum SGD in the area of September 2010 from a model mixture of different isotopes of Ra. This mixture model developed by Moore (2003), is based on a binary mixture between SGD and sea water (sea), and allows to calculate the fraction of groundwater ( $f_{SGD}$ ) from the equations (7):

$$f_{sea} + f_{SGD} = 1$$

$$f_{sea}^{224} Ra_{sea} + f_{SGD}^{224} Ra_{SGD} = {}^{224} Ra_{average} \cdot e^{\lambda_{224} \cdot T}$$
(7)

where  $\lambda^{224}$  is the decay constant of  $^{224}$ Ra (0.1894 d<sup>-1</sup>),  $^{224}$ Ra<sub>average</sub> the average activity of  $^{224}$ Ra (weighted according to depth) in the study area in September 2010 (1.5 ± 0.8 dpm·100L<sup>-1</sup>),  $^{224}$ Ra<sub>sea</sub> activity in the offshore sample (0.6 ± 0.1 dpm·100L<sup>-1</sup>) and  $^{224}$ Ra<sub>SGD</sub> activity measured in groundwater discharge to the sea. Given the piezometers made, from the linear regression shown in Figure. 23 and assuming that the groundwater discharge to the sea with a maximum of 36‰ salinity, the activity of  $^{224}$ Ra in this groundwater that discharges to the sea (salinity 36‰) and that could be used as "end-member" in the calculation, the groundwater discharge to the sea would be of 580 ± 30 dpm·100L<sup>-1</sup>.



**Figure. 23:** Activities (dpm·100L<sup>-1</sup>) of <sup>224</sup>Ra in water from different springs, boreholes and piezometers sampled. <sup>224</sup>Ra activities measured at sea are differentiated. The dashed red line represents the linear fit of <sup>224</sup>Ra versus piezometers salinity.

It should be noted that the residence time (T) of water from continental origin in the study area is another important parameter of Equation 2, which can be estimated from the differences in decay between  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$  (Moore , 2000). However, considering that  $^{223}\text{Ra}$  levels measured in this study are below the detection limit of the technique, it requires an alternative estimation of this parameter. Considering a water residence time in the study area of 1 day (minimum residence time that can be calculated with Ra isotopes and allows a maximum SGD flow in quantifying (Garcia-Solsona et al., 2010b), the maximum fraction of SGD (f<sub>SGD</sub>) in the study area is less than 0.0023, with an uncertainty similar to its own value, because the concentrations of  $^{224}\text{Raaverage}$  and  $^{224}\text{Rasea}$  are statistically equal.

However, and considering the fraction of continental water ( $f_{SGD}$ = 0.0023) like a maximum value, the discharge of groundwater in the study area can be determined from the equation (8) described by Moore (2003):

$$SGD\left[m^{3} \cdot d^{-1}\right] = \frac{f_{SGD} \cdot V\left[m^{3}\right]}{T\left[d\right]}$$
(8)

where V is the volume of water in the area studied (3.11 m $^3 \cdot 10^8$  m $^3$ , the zone outlined in Figure 22) and T is the minimum residence time of water in area of interest (1 day for Ra method). From this equation, the estimated maximum discharge SGD (mixture of fresh and salt water) into the sea is 130 hm $^3 \cdot y^{-1}$ .

Given that the salinity of the water considered is 36 ‰, only a small fraction of this is fresh water. Knowing minimum salinity of the wells sampled (0.4 ‰), the salinity of seawater (36.5 ‰) and those of groundwater that discharges to the sea (36 ‰), we can determine the fraction of freshwater in SGD ( $f_{gw} = 0.013$ ). From this value, and from the total discharge is obtained by equation 3 in September 2010, a maximum flow of fresh groundwater discharge to the sea of 1.7 hm³-y⁻¹ is extrapolated.

It should be noted that this flow only refers to the defined area (between Maro and Cerro Gordo). However, the results of the analysis of <sup>224</sup>Ra in the tip of the Mona and <sup>222</sup>Rn transect between Punta de la Mona and Cerro Gordo, suggest that groundwater discharge to the sea that could take place in this area is also very low. Nevertheless, it is important to note that the calculated flows derived from a sampling punctual on time, from which, discharge flows were extrapolated over a year. To obtain more precise measurements more continuous sampling should be prompt in time.

The maximum value of 1.7 hm<sup>3</sup>·y<sup>-1</sup> obtained in this study is much lower than the 7.9 – 11.5 hm<sup>3</sup>·y<sup>-1</sup> reported in Andreo et al. (2010) and Carrasco et al. (1998) at 100m over the sea level. From the management point of view, although the extraction of groundwater for drinking or turistic pruposes could be considered, could be prioritare to manegament the Maro spring or in any case supply water from the desalination plant of Marbella (55 km souther than Málaga) that, at full performance, obtains 20 hm<sup>3</sup>·y<sup>-1</sup> from seawater and Atabal's plant (next to Málaga) is allowed to produce up to 60 hm<sup>3</sup> y <sup>1</sup> water resources. The urban water supplies in Málaga are estimated to 156.93 hm<sup>3</sup> y<sup>-1</sup> (Durán Valsero, JJ., 2007) so that maximum value of 1.7 hm<sup>3</sup>·y<sup>-1</sup> is the insignificant 1% of the total. Moreover the explotaion of the coastal aquifers could be an environmental risk from two points of view. From the one hand, nutrients inputs from groundwater to the sea will be reduced and the biodiversity of this marine ecosystem area, which is protected by the Junta de Andalucia as an environmental reserve, could be affected and on the other hand the extraction of water from a coastal aquifer could be reduced the piezometric level favoring the seawater intrusion that is always an important hydrogeological and environmental problem. On the same way, it has to be thought that in the "Proyecto de Plan Hidrológico de la Demarcación Hidrográfica de las Cuencas Mediterráneas Andaluzas" is analised the quantitative, chemical and global state of Andalucian aguifers and it is concluded that they are not healthy due to the over-explotation of aquifers, saltwater intrusion and urban pollution. Even though, desalination plants are a good source of water, this management may derive to a salinization of the aquifer. This is a process with difficult recuperation and this delicate use of the coastal aguifers should be well studied.

# 5. CONCLUSIONS AND FURTHER PERSPECTIVES

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#### 5.1. CONCLUSIONS

Ra concentrations in the coast between Maro and Almuñécar are statistically comparable to the concentrations in open water, which makes difficult an accurate estimate of groundwater discharge to the sea, but evidence that in case of discharge it is not volumetrically important. This affirmation is corroborated with <sup>222</sup>Rn sampling, which also showed that the contribution of groundwater input in the study area is minimal. Despite the statistical limitations of the Ra technique, the sampling of September 2010 has estimated a maximum groundwater discharge to the sea of 1.7 hm³·y⁻¹ between the coast of Maro and Cerro Gordo, using <sup>224</sup>Ra as tracer.

Due to the low fresh groundwater that discharge to the sea compared with other close springs or desalination plants production and due to the salinization risk and the decrease of nutrients supply to the sea the explotation of the Alberquillas aquifer could be a future problem for the region.

#### 5.2. FURTHER PERSPECTIVES

More works might be done in focussing the points of discharge because knowing the important "end-members" is fundamental for estimating SGD. A precise study of the possible end-members of Ra in the area (e.g, sediment, subterranean aquifer...) would be interesting and working with the variation of the concentrations of Ra isotopes in the end-members based on the piezometric levels of the area, too.

Analysing the role of the Miel river might be crucial for analysing the nutrients flow to the sea, the total surface discharge and the lenght of the river mouth. Even, a management of its fresh water maybe could be considered. In relationship with this study of Miel river, the impact of  $f_{\rm SGD}$  to the area by analysing the nutrients could be courious because if the groundwater discharge is exploited, a lower quantity of nutrients would go to the sea thus the ecosystem would be damaged.

Finally an example of meteorological-SGD study might be done by comparing the discharge with the rainfall regimes and viewing the variability of the discharge from meteorological parameters.

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