Water Source Allocation and Numerical Water Quality Modelling in Roxo Reservoir Catchment, Portugal

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by

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Abstract

This research focuses on the water source allocation in streamflow components of the Roxo catchment utilising two tools. The objective of which is to determine their applicability in understanding hydrological processes and water source partitioning in a mesoscale semi arid catchment. Firstly a stable isotope analysis framework and a two source mixing model are utilised. Secondly the results of RAM component of the DUFLOW Modelling Studio (DMS) simulation are used. Stable water isotopes because of their fractionation, abundance and conservative nature, are able to preserve the characteristics of the hydrological cycle even in mesoscale catchments. They are able to give an insight into the intrinsic processes and a physical representation of the physical processes within a hydrological system. This is an element that has not yet been addressed in previous studies in the Roxo catchment. Moreover the RAM component of the DMS model has not been used for source allocation. This combination is a first step towards determination of a way to eventually parameterise and calibrate the RAM model for the catchment.

The isotope results show that there is an exterior recharge source to the water streams to those that are presumed present in the northern Pisoes subcatchment. The isotope determined contribution to the Roxo Reservoir inflow point at A28 in the southern sub-catchments from precipitation and groundwater were 43% and 57% respectively. The most contributing source in the different subcatchments is groundwater where contribution ranges 57-73% from the dry to wet season. Major hydrological process determined in the catchment was very high evaporation in the Roxo reservoir, the southern streams and open groundwater wells and mixing of different water discharges in the northern subcatchment around A23, A24, and A25 in stream network. Precipitation effects are overweighed by evaporation processes and mixing in the reservoir brings an almost uniform isotopic composition. The identified fault escarpment (Gabbros of Beja Aquifer System) in the northern subcatchments is attributed to the effect on streams in the region due to its inflows that have stronger effect than the evaporation and precipitation taking place. The isotopic two source mixing model proved too simple to describe some source contributions from northern subcatchments and mixing processes in the Roxo Reservoir as it omitted fractionation processes. Therefore a multiple source mixing model needs to be used in isotopic analysis.

RAM DMS a numerical model simulates the rainfall runoff discharge based on surface and weather forces and Meteosat MSG-MPE precipitation data. The contribution from groundwater discharge was calculated to be highest (87%) compared to other streamflows, which agrees in order of magnitude with that determined through isotopic method. However much more RAM model parameterisation needs to be done and refinements made in order to be able to distinguish the sub processes in the different sub catchments. It was possible to estimate the portion for water discharge that emanated from surface runoff, groundwater and subsurface runoff from the different surfaces. In the southern part of the Roxo catchment, the contribution due to runoff (2%) is less than in the northern part (7%). This is not derived by the isotopes so a combined system is more useful.

Future research should use an increased number of sample points for isotope data collection and could also incorporate remote sensing data for the estimation of parameters such as evapotranspiration and soil moisture. Combined with a further refined DMS numerical modelling it is will be possible to determine the exact source areas using the stable water isotope compositions as the signature of the water sources. Uncertainty estimation of both models used should also be carried out in further research.

Key words: source allocation, stable water isotopes, water balance processes, RAM DMS model

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This piece of work is dedicated to my loved ones, future family and those that have helped me get where I am……
……..I am sure they know themselves.

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List of Acronyms

LMWL	Local Meteoric Water Line
GMWL	Global Meteoric Water Line
LEL	Local Evaporation Line
GNIP	Global Network of Isotopes in Precipitation
COTR	Centro Operativo e de Tecnologia de Regadio (Operating Center and Irrigation Technology
IAEA	International Atomic Energy Agency
WMO	World Meteorological Organisation
V-SMOW	Vienna Standard Mean Ocean Water
WWTP	Waster Water Treatment Plant
DMS	DUFLOW Modelling Studio
DUFLOW RAM	DUFLOW Precipitation Runoff Module
ITN	Instituto Tecnológico e Nuclear (Nuclear and Technological Institute)
MSG	Meteosat Second Generation
MPE	Multi-Sensor Precipitation Estimate
IWD	Inverse Distance weighted Interpolation

1. Introduction

1.1. General water quality statement

Globally, the proportion of the population with access to improved drinking-water sources increased from 76% to 86% between 1990 and 2006 (WHO, 2009b). However high quality freshwater is limited in quantity and its quality is under constant pressure. Preserving freshwater quality is important for drinking water supply, food production and recreational water use (WHO, 2009a). Need for effective water management goes without saying and several hydrological parameters and water cycle components therefore need to be well understood for such an exercise to materialize. An increasing demand for the water resources is placed on the need to have specific hydrometric information to understand the water dynamics, origins and sources, in order that the world's water resources may be managed more efficiently with adequate data (Herschy, 1999). However, today there are several tools that allow making an appropriate assessment of the water resource.

An increasingly relevant tool in the study of the origins and the dynamics of surface water is the use of stable isotopes of oxygen and hydrogen incorporated in water molecules (Carreira et al., 2009). Several published researches have highlighted that isotopic studies have been useful in hydrology studies. For more than 30 years the stable isotopes have been used to study the hydrological regime of reservoirs, seas and catchments and their response to environmental changes (Froehlich, 2000). The basic understanding of the hydrologic conditions and stable isotopes Deuterium (δ^2H) and Oxygen 18 ($\delta^{18}O$) is necessary for water environmental studies as Dincer (1968) noted that the close relation of the isotopic and the hydrological cycle.

Other important procedure with particular potential in the aquatic ecosystem assessment is the use of hydrological modeling. In general, aquatic environments ecology and water balance are strongly regulated by inputs of river water and associated nutrients and suspended matter (Wolfe et al., 2007). Decisions about water pollution and management are mainly based on the use of model predicted flow and water quality trends (Manache and Melching, 2004). It is therefore important that before the models can be implemented they can still be evaluated, calibrated and validated to ensure their usability. Thus, water quality models can be very valuable tool in the management of water since they can simulate the potential response of different aquatic systems (WHO, 1997).

Dry land river systems are complex to understand for the water quality manager due to the variable rainfall events, river flow, high evaporation rates and high evapotranspiration (Ingraham et al., 1998). This is coupled with the mix of local and regional catchments runoff, and therefore in order to separate the different contribution and enhance understanding of the complex dryland hydrological processes taking course in the catchment, isotopes and hydrochemical ions are analysed and a numerical model results linked to this. Roxo catchment, located in Alentejo region Portugal is a semi arid catchment with large water requirements for irrigation and drinking water, which keeps the interest of assessing hydrological and hydrochemical behaviour, on especially the Roxo reservoir present in the area.

In this light, with the use of stable water isotopes, it is possible to determine hydrological processes influencing the water balance in any catchment or water body. Besides, characterising the isotope compositions and determining the important hydrological processes controlling water balance, isotope composition of the stream flow component of the water balance will be integrated into water source allocation techniques and, DUFLOW Modelling Studio (DMS) RAM water quality model results used to the same effect. This study hopes to certify the model prototype and be able to have a technique of water source allocation in any yet still complex mesoscale catchment which can be useful in routine water quality surveys.

1.2. Statement of problem

The pathways that water may follow through a catchment and their reactions with the environment always are varying (Church, 1997). Merely deriving quantities might be inadequate information as many processes can lead to the same output (Beven, 2002; Beven, 2006) in (Stadnyk-Falcone, 2008). Therefore accurate identification of hydrological flow paths processes and source areas in a catchment are crucial in managing water quality in any catchment. The general tendency when models are used is to determine how the model accurately predicts flows and quality. However some scientists (Kirchner, 2006) still emphasise the need to determine how models account for the processes taking place in hydrological system.

In the case of Roxo catchment, Portugal, most the studies are related with quantification of contaminants, especially in the Outeiro sub catchment and the main reservoir (Chisha, 2005; Vithanage, 2009). However, several transport processes (runoff) or subflows (direct interception of precipitation, surface flow or groundwater flow) operating in the catchment is a more difficult question. To be able to understand the relative importance of each of these paths and processes throughout the catchment it is essentially important to have knowledge of hydrologic flow paths, the role of the chemical and isotopic composition in the water resource cannot be ignored.

Reservoir water balance, (Vithanage, 2009) was defined as having a simple basin inflow. The inflow to the reservoir was not defined as to where it originated from in the catchment, and no separation between storm surface runoff and groundwater flow was made. Groundwater contributions are much more difficult to quantify and these in several water quality studies have always been assumed to be small relative to other contributions. This is not necessarily accurate as Sen and Gieske (2005), predicted ground water surplus for flow and a recharge zone in the catchment. The identification of source areas is made even more crucial as the role of seepage in water quality or lakes and rivers is important at it can be source of nutrients for algae growth (Brock et al., 1982; LaBaugh et al., 1997) which is already a reported problem in Roxo catchment .

Justification to carry out this study was based on the defined water quality problems and the necessity to know how external hydrological fluxes affect within reservoir and stream characteristics and processes in water resources management. It was identified important to first understand hydrological processes directly affecting the water balance and in reservoir fluxes using isotopes. Then an assessment of the importance of various water sources determination in whole Roxo catchment was undertaken using stable water isotopes and numerical DUFLOW RAM model to evaluate the applicability.

1.3. Objectives

The main objective of the study is to use stable water isotope data to better understand the relative importance of hydrological processes (such as rainfall, surface runoff, groundwater base flow (seepage) and evaporation) that can control the water source allocation of the Roxo reservoir and contributing streams, and combine with the study of numerical water quality modelling to determine possible water sources.

For this the following specific objectives were worked on:

1. Determination of isotopic framework of Roxo catchment for analysis and interpretation of the spatial and temporal distributions of stable water isotope data in the Roxo streams and reservoir
2. Interpretation of the water source allocation /contributions from the different parts of water balance and importance to Roxo reservoir catchment
3. Assessment and allocation of water source contribution from the various catchments using DUFLOW RAM model
4. Comparison isotope water source allocation method results and the DMS (MSG MPE driven DUFLOW RAM model) source allocation method results

1.4. Research Questions

To this effect it is important to address the following research questions:

1. How stable water isotope components are spatially distributed in the different parts of Roxo catchment water balance system (surface waters, groundwater, and reservoir).
2. What are the important hydrological processes in the catchment water balance
3. How much is the contribution of the water balance components using stable water isotope ratios to the Roxo reservoir water
4. What is the contribution of the runoff subflows components to the water inflow and balance of the Roxo reservoir using DUFLOW RAM?
5. What and how much is the runoff source contributions from the different sub catchments to the Roxo Reservoir?
6. Can a combined use of stable water isotope data and the DMS model rainfall - runoff modelling results improve our understanding of water source allocation and water balance processes in the Roxo catchment

1.5. Hypothesis

The hypothesis which is formulated to underpin this research is related to an improved methodology for environmental assessment and can be phrased as follows:- the use of stable water isotopes tracers in combination with standard hydrological datasets and satellite rainfall data, can improve semi-distributed catchment water flow process understanding and modelling in terms of sources and pathways.

1.6. Description of Study Area

Roxo catchment is located in Beja District of Alentejo Province, in southern Portugal. The catchment's Roxo reservoir has high economic importance as the water is used for irrigation and public water supply purposes. The geographical location of the catchment ranges from 37º46'44.40'' N to 38º02'39.39'' N in latitude and from7º51'47.93' W to 8º12'24.67' W in longitude in which lies the Roxo reservoir the dam is 37º55'48'' N and 8º6'9' W. The Figure 1-1 below shows the location of the Roxo catchment which covers an area of 353.18km^2. Several studies have been carried out in the Roxo catchment and in these the climatic data has been discussed (Cherie Mekonnen, 2005; Chisha, 2005; Ricardo Rodriguez, 2003; Sen, 2004; Sen and Gieske, 2005; Vithanage, 2009). Close to the Roxo reservoir catchment are Beja and Aljustrel automatic weather stations whose data can be obtained from the COTR site, this data is used to define the weather conditions.

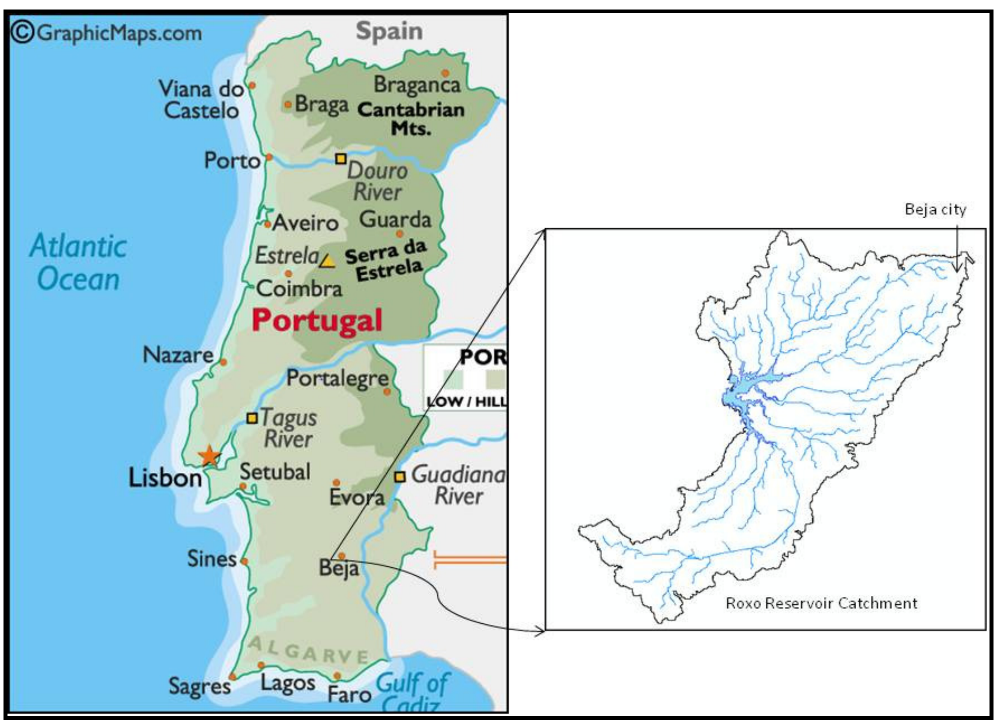

Figure 1-1: The Location of Roxo Reservoir Catchment In Portugal
http://www.worldatlas.com/webimage/countrys/europe/lgcolor/ptcolor.htm

1.6.1. Climatic and Weather conditions

The area has a predominantly Mediterranean climate with average annual temperature of about 23 ºC with the average monthly temperate in summer (June to September) is about 23.33 ºC for Aljustrel and 23.12 ºC for Beja Station. August is the hottest month with an average monthly temperature of 33 ºC. Minimum temperatures are recorded in the months of December and January (winter season) when the average monthly temperature is about 10ºC. The temperature variations of the year 2009 are used for description of the general climatic variables and these are shown in the Figure 1-2 below.

The study area receives rainfall during winter as indicated in the Figure 1-2 below with very little or no rainfall during summer especially June to September. Maximum monthly precipitation occurs in October and can be up to minimum 103 mm for the month. Dry months occur from May to September where there is little precipitation in September and this associated with high ET (10mm/day).

1.6.2. Land Use

Main land use is agriculture and crop types that are grown are maize, wheat, sunflower and olives. Coniferous forest plantations are also observed, as well as eucalyptus forests in the southern part of the catchment. These land uses have been discussed in the fieldwork section further on.

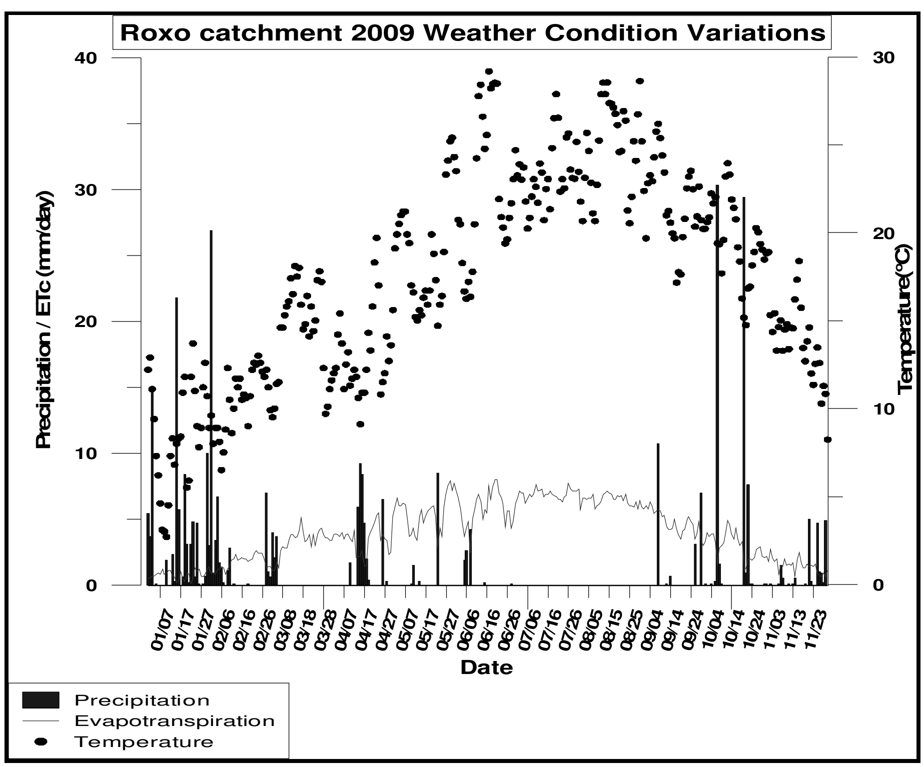

Figure 1-2 : Variation of precipitation and temperature and ETo in Roxo catchment in 2009 (Beja station data on www.cotr.pt)

1.7. Thesis Structure

The thesis organisational structure is outlined below to be able to give the reader an idea of what is in each chapter.

Chapter 1: Introduction

This chapter introduces the research as well as defining the research objectives and motivation of the research. The study area is briefly described in the chapter as well just to update some information from previous literature.

Chapter 2: Review: Stable Water Isotope and DUFLOW Modelling

A review of literature that describes the concept of the use of isotopes in hydrology for source determination and also for understanding hydrological processes is included in this chapter. It also includes the concepts behind the DUFLOW model and sites a few of the equations that govern it

Chapter 3: Materials and methods of data analysis

Data used is described; the data collection and the research implementation, in terms of the analysis methods is also incorporated in the chapter.

Chapter 4: Stable Water Characterisation and Source Allocation

The isotopic results are reported in this chapter and interpreted to answer some research objectives and questions.

Chapter 5: Numerical Water Quality Modelling and Source Allocation

The results and discussion of the analysis done on the Ram model output are shown in this chapter.

Chapter 6: Conclusions and Recommendations

The conclusions in terms of the source allocation are commented on and the concluding remarks on the applicability of these two methods to determine source allocation in a mesoscale catchment as Roxo.

2. Review: Stable Water Isotope and DUFLOW RAM Modelling

2.1. Stable Water Isotope

An isotope is defined as a species of a given element, differing from another of the same element by the number of neutrons. Isotopes of hydrogen are the common stable hydrogen, deuterium (^2H or D) and radioactive tritium (^3H) whilst those of oxygen are normal oxygen 16, a rare heavy oxygen 17 then heavy oxygen 18. Since Hydrogen and Oxygen make up water, the different combinations of these isotope constituents can be expected and it is on this basis that the water can be termed heavy or light (Mazor, 1991). $H_2{}^{16}O$, $H_2{}^{18}O$ and $^1H^2H^{16}O$ (Araguás-Araguás et al., 2000) are the three out of nine isotopic water molecules that occur in nature in concentrations that can be measured. These stable water isotopes can be used in the understanding various hydrological processes.

2.1.1. Standards Used for Oxygen and Hydrogen Isotopes

Ocean water is used as the standard for all H and O isotopes analyses as developed by Craig (1961). The standard called the Standard Mean Ocean Water (SMOW) is used as the Craig standard but however an equivalent was developed by Vienna group named Vienna Standard Mean Ocean Water (V-SMOW). The isotopic ratios of VSMOW were found to be equal to $^2H/^1H$ = $(155.95^+/-0.08)*10^{-6}$ (Wit et al., 1980) and $^{18}O/^{16}O$ = $(2005.20^+/-0.45)*10^{-6}$ (Baertschi, 1976). Conventionally isotopic composition results are expressed using the delta (δ) notation, representing a difference in units per thousand (denoted by per mille (‰))relative to VSMOW (Craig, 1961; Mazor, 1991). Indicated in equation 1 is the formulation of the isotopic ratios of Deuterium and Oxygen 18 respectively

Δ (δ) is calculated by ;

$$\delta_{sample/s\tan dard}\left({}^{o}\!/_{oo}\right) = \left(\left({}^{R_{sample}}\!/_{R_{s\tan dard}}\right) - 1\right) \times 10^3$$

Equation 1

Where R is ratio of h**e**avy to light isotopes or either Hydrogen or Oxygen in sample and standard respectively, as defined in the equation 2 and 3 below.

$$\frac{^2H}{^1H} = R_H$$

Equation 2

$$\frac{^{18}O}{^{16}O} = R_O$$

Equation 3

Interpretation is based on that a positive delta value means that the sample isotope ration is higher than that in the standard and the opposite is true for the negative values.

Stable isotope studies are based on the tendency of isotope pairs to fractionate into heavy and light. Fractionation occurs when some hydrological processes such as evaporation and condensation (Fetter, 2001; Gibson and Edwards, 2002; Kendall and McDonnell, 1998; Mazor, 2003). In evaporation, lighter isotopes are preferentially evaporated over heavier ones and in condensation, the heavier water vapour undergoes condensation more efficiently (Mazor, 1991). This fractionation concept gives a very powerful tool for tracking hydrologic phenomena such as evaporation. Precipitation can be characterised too using the fractionation concept. This can also be referred to as the rate at which the moisture is taken out or rain out (Carreira et al., 2009) from the moisture source to the site of precipitation, and this describes some empirical relations that then define the effects of things like the altitude, distance to the coast, altitude and others.

2.1.2. Global Meteoric Water Line

Studies done from as early as 1961, determined the relationship between deuterium and oxygen-18 concentrations in natural meteoric waters from many parts of the world. In these cases the isotopic content were determined with a mass spectrometer (Craig, 1961) "Meteoric water" refers to long standing water in the ground which originates from precipitation (American Meteorological Society, 2000) is used in the field of isotopic. Craig (1961) made an assertion in his research that isotopic enrichments relative to ocean water, display a linear correlation over the entire range for waters which have not undergone excessive evaporation and this defined the Global Meteoric Water Line (GMWL). The GMWL was defined by the use of 400 water samples for the rivers, reservoirs and precipitation from various countries that were fit on a line of best fit of $\delta D = 8\delta^{18}O + 10$.

Monthly precipitation samples of any region give rise to the Local Meteoric Water Line (LMWL) (Karim and Veizer, 2002) and this together with its relationship with GMWL is useful in explaining the relationship of the water and respective hydrologic processes. LMWL is useful and convenient way of understanding local water movements and sources or origins and processes under which the water has been subjected. Deuterium excess ($d= \delta D - 8\delta^{18}O$)also used to explain the changes in the isotope composition from the line with slope of 8 going through the Vienna SMOW (Dansgaard, 1964).

2.2. Isotope Water Source Allocation Methods

There are variations in the isotopic content of precipitation however this can eventually reach uniformity with ground water in time and space after passing through the vadose zone. All the same, a level of temporal variability in the isotopic composition ratios (δ) of precipitation relative to the soil and groundwater exists. The differences existence of the differences between these results on distinction between event water and pre event stored) water in the catchment (Kendall and McDonnell, 1998). It is this difference that can be used as tracer in separating storm flow hydrograph into its event and pre event components in understanding the water balance. All these factors make use of stable water isotopes (δ2H–δ18O) as notable tool for study of runoff generation processes and water balance from different water bodies in seasonal environments (Brock et al., 2007; Gibson and Edwards, 2002; Wolfe et al., 2007). Studies of stable isotopes for environmental studies and water balance have had several important applications in different catchments (Gibson and Edwards, 2002; Gibson et al., 2002; Karim and Veizer, 2002; Prowse and Prepas, 2007). Among these several Isotope based approaches for water balance assessment in Canada (Gibson et al., 2002). Isotopic studies are useful in the identification of recharge area in water systems, and to investigate the origin and interconnection of water bodies (Carreira et al., 2005) overall and this is applicable in the Roxo catchment. By superimposing both stable water isotopes as key component isotope labelling of both precipitation and evaporating surface water bodies, this is achievable.

Water source allocation has been studied in several catchments with the application of mixing models (Meredith et al., 2009) such as those applied later on in the research. This assumes that the water is completely mixed in the water mixture of interest, that the sources have different isotopic signature as the mixture and from each other (McKechnie et al., 2004; Meredith et al., 2009; Wilcox et al., 2004) the method is described in chapter 3 section 3.9.

Isotopic framework utilised for the determination of the water balance hydrological processes revolves around the interpretation of Local Evaporation Line (LEL) (Wolfe et al., 2007). A LEL is a useful way for determining the evaporation processes that would have occurred to the various water sources. LEL is defined by a regression line through isotopic compositions of evaporating surfaces of catchment water samples collected.

The most essential highlight is that stable water isotopes aim to integrate small scale variability (Kendall and McDonnell, 1998), resulting in an effective indication of catchment scale processes through their interpretation. However explanations of stream hydrochemical behaviour will continue to require careful integration of results from the hydrometric, isotopic and geochemical methods rather than the use of any approach in isolation and this has to be taken care of in any research.

2.3. Isotope studies in Roxo Catchment

Stable water isotopic studies in the southern Portugal of the Alentejo province have focused on the ground water aquifer recharge studies (Galego Fernandes and Carreira, 2008; Paralta and Oliveira, 2005) and on isotopes in precipitation (Carreira et al., 2009; Carreira et al., 2005). An extensive study of the Iberian Peninsula collaboration WMO and IAEA, in the project GNIP (Global Network on Isotopes in Precipitation) was one of the first studies done in the Portugal regions for the acquisition of background information essential for climatological and hydrological investigations with the main scope on water resources planning and development. This database provides precipitation isotope ratio data recorded over a period 1988-1991 for Beja. This same information is used by Carreira (2005) in a study of the Portugal isotopes in precipitation framework as part of an extensive study that covered the entire Iberian Peninsula rather than on smaller catchment scale. This research will make use of collected isotopic data in the Roxo catchment area in Portugal to study, water balance processes and determine source of subflows.

2.4. Numerical Water Quality Modelling

Numerical models are mathematical models that use a numerical time stepping procedure to obtain the behaviour over time (SERC(Science Education Research Centre), 2009). More like giving a time rate change over time and this can be defined using differential equations. These are solved to result in a numerical solution.

2.4.1. Water Quality Modelling

Stream and reservoir water quality are important phenomena that need to be studied. However for such to be accomplished, in the streams its also important to understand the water flow and transport of constituents water processes such as nitrification and dispersion Water quality can be modelled in close to realistic way for environmental studies. In this research the DUFLOW model is used in this case as it has a flow and water quality component and it is explained later on in the chapter.

Model performances can be evaluated with the availability of similar observed values. The comparison of the predicted and the observed means using

- The Nash Sutcliffe modelling efficiency (E) Nash and Sutcliffe, 1970,
- The RMSE can also be used
- and the other methods such as the regression coefficient R^2 and
- The PBIAS (Percent Bias) can also be used in model efficiency analysis following Equation 2 by Morias et. al, (2007)

2.4.2. DUFLOW Modelling Studio (DMS)

DUFLOW model package is a one dimensional flow and quality model (STOWA, 2004). It is important in that it allows modelling the transport, describing processes and interactions of pollutants (Mwanuzi et al., 2003). DUFLOW flow simulation is based on the one-dimensional partial differential equation (Saint-Venant) that describes non-stationary flow in open channels (STOWA, 2004), solved numerically. In the DUFLOW model it is possible to schematise the structure of the river network even including the artificial structures such as the irrigation channels and canals and weirs.

The state variables or the core variables in the DUFLOW model are the H: water levels, Q: the flow discharges, U: the water flow velocity, C: the substance concentration and the F: the substance loads.

2.4.2.1. DUFLOW Water Flow model

The flow model is governed by the Saint-Venant one dimensional differential equation that describes non-stationary flow in open channels (STOWA, 2004), solved numerically.
Several assumptions consider for St. Venant equations:

- Flow is one-dimensional
- Hydrostatic pressure prevails and vertical accelerations are negligible
- Streamline curvature is small
- Bottom slope of the channel is small
- Manning equation is used to describe resistance effects
- The fluid is incompressible (Merwade, 2005)

These equations, which are the mathematical translation of the laws of conservation of mass and of momentum are highlighted in equation 4 to equation 6 below adopted form STOWA (2004):

Mass equation

$$\frac{\delta B}{\delta t} + \frac{\delta Q}{\delta x} = 0 \qquad \textbf{Equation 4}$$

Momentum equation

$$\frac{\delta Q}{\delta t} + gA\frac{\delta H}{\delta x} + \frac{\delta(\alpha Qv)}{\delta x} + \frac{g|Q|Q}{C^2 AR} = a\gamma w^2 \cos(\Phi - \phi) \qquad \textbf{Equation 5}$$

Discharge equation

$$Q = v * A \qquad \textbf{Equation 6}$$

Where:

t	time [s]
x	distance as measured along the channel axis [m]
H(x, t)	water level with respect to reference level [m]
v(x, t)	mean velocity (averaged over the cross-sectional area) [m s-1]
Q(x, t)	discharge at location x and at time t [m3 s-1]
R(x, H)	hydraulic radius of cross-section [m]
a(x, H)	cross-sectional flow width [m]
A(x, H)	cross-sectional flow area [m2]
b(x, H)	cross-sectional storage width [m]
B(x, H)	cross-sectional storage area [m2]
g	acceleration due to gravity [m s-2]
C(x, H)	coefficient of De Chézy [m1/2 s-1]
w(t)	wind velocity [m s-1]
Φ(t)	wind direction [degrees]
ϕ (x)	Direction of channel axis, measured clockwise from the north [degrees]
γ (x)	wind conversion coefficient [-]
α	correction factor for non-uniformity of the velocity distribution in the advection term, defined as:

Equation 4: Correction factor for non-uniformity of velocity distribution

$$\alpha = \frac{A}{Q^2} \int v(yz)^2 \, dydz$$ **Equation 7**

A cross-section [m^2]

The mass equation states, if the water level changes at some location this will be the net result of local inflow minus outflow. The momentum equation expresses that the net change of momentum is the result of interior and exterior forces like friction, wind and gravity. For the derivation of these equations, it has been assumed that the fluid is well mixed and hence the density may be considered constant (STOWA, 2004)

2.4.2.2. DUFLOW Water Quality model

For the transport model (water quality model), a one dimensional advection-dispersion equation is used. The general transport equation used in water quality model prototype is:

$$\frac{\delta (BC)}{\delta t} = -\frac{\delta (QC)}{\delta x} + \frac{\delta}{\delta x}(AD\frac{\delta C}{\delta x}) + P$$ **Equation 8**

Where C is the constituent concentration (g/m^3)

Q is flow (m^3/s)

A cross sectional flow area (m^2)

D dispersion coefficient (m^2/s)

B cross sectional storage area (m^2)

x x-coordinate(m)

t time(s)

P production of the constituent per unit length of the section (g/m.s)

Description of water quality is defined at the predictions of the loads of Ammonium, Nitrate and Phosphate. The load (F) is estimated in the model using the simple relationship as the product of concentration (C) and the calculated discharges(Q) in the relationship ; F= Q x C (Mannaerts, 2009). The first term in the Equation 8 described the advection part of the transport system that caters for the amount of a pollutant that is taken with the flow in the stream. The second part deals with the dispersion which defines the eddy transport and transport derived smoothening of concentration gradients in the lateral and vertical directions.

The last term of the equation, is important in the water quality project as it accounts for all the biological, chemical and physical processes to which the constituent is subjected. These control the fate and behaviour of the constituents. The transport of nutrients can be modelled through DUFLOW user defined quality models. In this study is modelled mainly focusing on the mineral N and all its forms and processes to which it is subjected, especially in nitrification (refer to previous section).

When the quality calculation is done, the water quality calculation can become unstable and the results could contain negative concentrations. This is as a result of having a very high peclet value of greater than 1.The peclet value is defined as the

$$Pe = \frac{v * \Delta x}{D}$$

Where Pe is the Peclet value [-], V the mean flow velocity (averaged over the cross sectional area)[m/s], and Δx is the section length(distance between two calculation points) [m], D being Dispersion coefficient[m2/s].The mean flow velocity V = Q/A where Q is discharge and A is cross sectional area. The solution to the problem of the Peclet number is found by reducing the section length or by increasing the dispersion (STOWA, 2004).

2.4.2.3. RAM (Precipitation Runoff Model) module

The RAM runoff processes (surface, interflow drainage or slow groundwater discharge) are all necessary to distinguish between them , to be able to correctly describe the water quality (STOWA, 2000).In the RAM the runoff surfaces are classified as

- Open water surface
- Paved surface
- Unpaved surface

These classifications are done in the view of the different runoff processes that can take place (STOWA, 2004).

Paved surface can be distinguished between paved surface in rural area, in urban area and in green house. In the rural area the runoff can easily be drained through ditches and on the outside of the paved area. In the urban areas in paved areas the drainage can be in through the sewer system and then some of the precipitation is stored on the street surface. On greenhouses, precipitation is discharged directly to the surface water even through any storage reservoir.

On Unpaved surface some processes are described and can be typical for such a surface. The three processes that can take place include infiltration into soil moisture, percolation into the ground and ground water discharge into drainage systems. The precipitation runoff processes within an unpaved catchment area are mainly determined by soil and terrain properties, such as slope and soil type. These properties may, however, also vary strongly within the defined catchment area and it is up to the user to define the differences in the catchments and split the catchment in a way as they wish. These can therefore be determined to be homogenous in particular catchments. The precipitation runoff processes within the ground water flow is partitioned in the fast and slow components.

RAM model involves the calculation of runoff discharge by form of the (linear reservoir mode

- Calculating the specific discharge at first over a time period maybe in mm/day
- Then it is then converted to discharge at a moment at a point in m3/sec

Based on the values of precipitation and evaporation, and the properties of the area object, the RAM will calculate the additional flow into the network at Area points. This is performed as by several governing equations until estimation of discharge from effective precipitation the discharge shown in equations below describing surface runoff discharge:

$$q_{sur,t} = q_{sur,t-1} e^{\frac{-\Delta t}{k_{sur}}} + P_{N,sur,t}\left(1 - e^{\frac{-\Delta t}{k_{sur}}}\right)$$

$$Q_{sur,t} = a \times A_{unpaved} \times q_{sur,t}$$

Where:

$q_{sur.t-1}$	as the specific surface recharge unpaved surface (mm/day)
$P_{N,sur,t}$	the effective precipitation surface runoff (mm/day)
$A_{unpaved}$	unpaved surface area (ha)
k_{sur}	Time constant reservoir surface runoff unpaved surface (day)
Δt	Time step (day)
α	Conversion factors [-] of 10/(24*3600)
$Q_{sur,t}$	surface runoff unpaved surface (m_3/s)

An adequate description of a precipitation runoff relationship in surface waters is also necessary for the prediction of water quality and the RAM component is useful for such a thing. It is useful to describe the various water sources and loading sources of pollutants into streams.

2.4.2.4. RAM (Precipitation Runoff Model) Water Quality model

The water quality module description is also governed by the discharge processes that are determined be it surface runoff, quick or slow groundwater discharge component. The quick and the slow were defined in theory due to the differences in the soil water processes and the characteristics of water quality. This is defined in the model with the concepts of linear reservoirs. The first concept is the parallel Nash Cascades and where both the slow and the quick are defined by a series or linear reservoirs. The second being the combination of Nash-cascade and the Krayenhoff van de Leur, in which for the Nash-cascade, is defined by parallel linear reservoirs and the later by series of linear reservoirs.

The RAM water quality component so far is defined for the Nitrogen and Phosphorous balance (STOWA, 2000). It is based on the illustrated concept in the chain below of;

Supply → Reaction Processes in the Soil → Discharge

The discharge with water is usually subdivided in runoff (surface runoff) and leaching (via ground water discharge). Open water surface effective precipitation is calculated as precipitation minus the open water evaporation. Similarly for the water quality as for the runoff it is strongly recommended to calibrate the model on measured concentration.

Drainage of nutrients and pollutants mainly occur through the discharge of precipitation in surface runoff and leaching (ground water discharge). The concepts of the processes that take place in the soil such as volatilization are also taken as the drainage and discharge of the P and N in other forms. RAM does not model the reaction processes in the unsaturated zone that are extremely complex (STOWA, 2000).

2.5. Water Quality Modeling Studies in Roxo Catchment

Water quality problems have been evidently identified and studied in the Roxo catchment. Most of the water quality models that were implemented for the Roxo catchment, as it is important to note, have not been calibrated and validated due to lack of data already existing. However several studies have been undertaken by the ITC and some of the relevant studies pertaining to water quality studies of this nature have been noted.

The level of the nutrient loads contributed by the Outeiro subcatchment is quantified and determined in the study by Chisha (2005). With the use of the GWLF model, critical source areas in the Outerio catchment were determined. This focused on nutrient pollution, expected nutrient loads, area coverage contributing to nutrient pollution mainly focusing study on the Phosphorus. The Water Quality Monitoring Station Analysis (WQMSA) model was also used in monitoring the water quality in the reservoir which could be used to monitor the water quality over space and time through its assistance is the establishment of representative sampling monitoring points. Concluded that agricultural runoff contributes more of the dissolved N loading of about 51% of the total N loadings into the catchment. Groundwater in resulted to contribution of 46% and urban runoff contributes about 0.12% of dissolved Phosphorous. Identified were the urban runoff, point source (from WWTP), agricultural runoff and groundwater sources.

Study by Gokmen (2006) was an evaluation of the inputs to the SWAT model setup and then several datasets were determined and collected. Some of this data is being used in this study to cover for the necessary data that's needed for the evaluation of model as well as the calibration and the validation of the DUFLOW model in question.

In complement to the water quality studies also important in this research is the study of water balance of an area. Sen and Gieske, (2005) studied water balance in Roxo catchment undertook a water balance study of the Roxo catchment which deduced a minimal contribution of water for the groundwater sources of the water balance. The surplus water available was calculated for the periods of October to November and not in any other period. Ground water flow was determined to be small and was concluded to have been notably influential in the Pisoes subcatchment.

The DUFLOW model work was initiated in 2009 (Vithanage, 2009), on the design of a flow and quality model prototype. Only the stream flow model was calibrated and analysed. For the developed prototype to be usable, as recommended, need was therefore for the model to be calibrated and validated and further analysis be done to some of the modules. This is what this research intended , to analyse the RAM outputs to determine water source allocations and couple that with interpretation of isotopes in refining the model prototype interpretation for use.

3. Materials and Methods of data analysis

3.1. Introduction

This chapter defines the methods and the materials that are necessary to attain the objectives outlined before. These include the drawing of the work plan, to the field data collection and several data sources description as well as the processing done after the fieldwork.

3.2. Work Plan

In order to achieve the research objectives and questions, number of activities had to be accomplished.

3.2.1. Pre field work

Before the fieldwork was done, relevant literature and some data was downloaded off websites:

- COTR (http://www.cotr.pt) for Climatic data download (air temperature, rainfall, ET).
- Isotope database of the IAEA/ WMO for isotopes in precipitation (GNIP).
- The CORINE Land cover map,
- EUMETSAT MPE downloads (Geonetcast toolbox),
- Aster DEM -DEM Extraction (ASTER DEM).

Thesis write up on some of the sections had to be initiated for the literature review, study area review, Fieldwork plan, sampling strategy.

3.2.2. Field work phase

Fieldwork period was from the 5th till the 20th of September 2009, during which samples and relevant ground data were gathered. Samples were taken within the catchment and in the Roxo Reservoir. Already established sampling sites were used for the sake of data consistency to enable comparisons with historical data. There were 22 sampling sites scattered over the catchment, see map in Appendix 1, of which 15 are for surface water and 7 are groundwater sampling wells. Some new sites were added to the earlier used sites. The details of field activities are described in section on fieldwork ahead in the chapter.

3.2.3. Post field work phase

The post fieldwork involved laboratory work of the water samples in the ITC laboratory, data compilation and preparation, numerical water quality model calibration and validation and isotope data analyses and conclusions. These are fully described in the upcoming sections of this chapter and chapters to the end.

3.3. GIS and Remote sensing data colection

Water quality modelling requires as many surface properties inputs as possible into the numerical model. The use of remote sensing data is important to get data for the catchments scale. ASTER digital elevation model (DEM) was used for catchment delineated and the Land Cover maps (CORINE land cover map), Multi-sensor Precipitation Estimates (MPE) data time series, soil maps for the Roxo catchment, soil properties. For verification only some of these remote sensing data was reanalysed if it were necessary to make changes in the remote Model inputs. The model prototype (Vithanage, 2009) was however adopted and slightly modified with these.

- 25 hectares (250 000m^2) CORINE land cover 2000. Although this is course resolution, for the purposes of the update and extension of the Duflow water quality model the CORINE land cover class map suffices.
- ASTER DEM with 30m resolution downloaded from (U.S.G.S., 2009) input into the extraction of catchments the analyses and hydroprocessing of the DEM Maathuis and Wang (Maathuis and Wang, 2006).
- The MSG MPE (METEOSAT Second Generation, Multi sensor Precipitation Estimate) (EUMETSAT, 200..... 2009), used the already processed daily sums of data for the ILWIS format. The data is already in mm/day format and which is the unit ready for use in the RAM component of DUFLOW (STOWA, 2000).
- Soil map for Roxo catchment obtained from COTR was analysed for any differences with the existent soil data and the other physical data was gathered from precious studies of Gokmen (2006) .

3.4. Field data collection

3.4.1. Field observations

Fieldwork was carried out for 2 weeks from the 5th till 20th September 2009 in Roxo Catchment, situated in the Beja district of Alentejo province, Portugal.

To familiarise and investigate the accessibility and state of water in the different streams and wells an initial survey was carried out in the catchment. The catchment was found to be generally very dry. Some rivers consisted only of water pools in the channel bed and some streams had dried-up completely or were running on very low base flow. The general notion of the local population was the water levels have been the lowest compared to previous years. It was therefore considered necessary to add some new sampling points in some areas. This depended on the availability of wells and their accessibility as some preferred locations were private property and locked off access. In terms of general water storage, some small ponds were identified which are utilised for irrigation and watering animals. During the field campaign a couple of days recorded a rainfall of up to 10mm. This however did not have any visible effect on the discharges as the ground had been parched for too long.

The main land use observed in the area of the catchment was agriculture. At the time of visit we observed young olive farms, harvested wheat, and alfalfa and sunflower fields. The identified irrigation systems were by overhead and drip irrigation, although there was not much activity during this period as it was harvest season. However it was difficult to identify wheat from alfalfa grown areas from the appearance of the harvested stalks. Some of the land had already been prepared for next cropping season and was bare. Several oak forest plots were observed and few of these had been harvested for the cork making. Livestock farming included sheep, goats and cattle and few pig farms. In some instances this was concentrated near water bodies. Also few vineyards were identified in the catchment area. Some natural forests and eucalyptus plantations were observed to be in the southern and the south eastern part of the catchment.

COTR offices in the Beja were visited briefly and several soil maps for the Roxo were obtained from the same offices as well.

3.4.2. Water sampling protocol

Water samples for isotope assessment were collected from 24 sites that include wells and streams and the Roxo reservoir. These sampling points are indicated in the figure in Appendix 1. Care was taken to maintain the same sampling points as of last season (April sampling campaign) very close for the use of comparing seasonal changes in processes as in the objectives. The added new points were labelled w 20, w19, w18, a36, a39. The activities that were maintained at each sampling point are listed below

- Determine geographic location coordinates using Garmin GPS in UTM coordinates
- Check the colour and smell of water to be sampled
- Study and document surrounding vegetation and land uses
- Rinse sampling bottle three times with sample water before finally collecting sample
- Filter samples with 0.45 µm Whatman filter for all water quality analyses including isotopes
- For isotope samples close immediately with double cap avoid vaporisation(50 ml)
- For other hydrochemical tests, the filtered sample was acidified with few drops of Hydrochloric (HCl) acid 30% Suprapur to pH=2
- Tightly close the sample bottles and label clearly
- Store samples in cooler box

All water samples for isotopic tests were collected, stored in air-tight 50 mL high-density polyethylene bottles. Evaporation of the samples was avoided as much as possible as highlighted by Mazor (1991) that evaporation could lead to erroneous inferences from isotopic enrichment during sampling. The stable isotope samples were sent to the Vienna Environmental Isotope Laboratory for stable isotope analysis using conventional standard methods and techniques.

Sampling for general water quality chemical parameters was carried out at 15 of the points strategically distributed in an attempt to cover the whole catchment. These were filtered through 0.45µm filter paper and preserved with hydrochloric acid and transported to ITC laboratory for analyses.

Physical parameters such as temperature, EC, pH and DO (Dissolved Oxygen) and alkalinity also including Chloride were analysed on site. The test kits were calibrated at the start of each day before any test could be done initially when calibrated the test kits were tested on fresh distilled water.

3.4.3. Land use classification and assessment

Random samples points were taken in the different parts of the catchment using a Garmin GPS and the data captured in an IPAC. The sampling almost covered the whole catchment where ground truth data was taken for land use classification and assessment of the land use classification that will be useful in the DUFLOW model. This will be applied to a land use classification of the CORINE map. Some pictures of observed land covers in the catchment are in Appendix 5

3.4.4. Stream Flow measurements

In numerical model DUFLOW used in this research, the stream discharge needs to be an input for at least the section systems. It is in this light that a salt dilution experiment was used to estimate the discharge and dispersion to update the DUFLOW prototype. This experiment measurement was performed one of the points on the Chamine (Pisoes) River at the sampling point A24 (of coordinate location 590483, 4203625). This point was chosen because which was flowing at a large enough stretch with no obstructions for the experiment so that all the stream properties could very well be estimated.

Stream flow estimation of was calculated using the dispersive solute transport and equations using data from set of harmless table salt dilution experiment method and the HACH EC meter. The amount of salt applied in the stream was 400g and 350 g respectively.
The measurements form the field are attached in the Appendix 6 .
The methods to further derive the parameters were

- using the 1D dispersive transport equations that is: Method applied by (Thomann and Mueller, 1987) in sample problem 2.6 here to calculate D coefficient
- The flow rate Q (m^3/s) was estimated using the mass conservation:

$$Q = \frac{M_{xo}}{\int_{to}^{\infty} \left(C_{(xi,t)} - C_b \right)}$$

Equation 9

Where M_{xo} salt load applied at the application point (g), $C_{xi,t}$ as the salt concentration at time "t" at the selected position(mg/l)

The Estimated dispersion 1.03 m^2s^{-1} and stream flow 2.27 ls^{-1} is which is way lower than previous year's flow of 0.12m^3/s (120 l/s).which was taken in the October month which is the beginning of the rainy season This however confirms claims of it being a generally dry year as the flow is very low consistent with the data obtained (Ricardo Rodriguez, 2003) during the period under analysis in the DUFLOW RAM simulations.

3.5. Hydrochemical Water Quality data

3.5.1. In-situ hydrochemical water tests

In situ water tests for the physical parameters as Temperature, Electrical conductivity, Dissolved Oxygen and pH and alkalinity (bicarbonates) as well as Chloride were carried out. These methods used have are highlighted in the Table 3-1 below. Prior to taking the measurements the sensor probe was calibrated with the standard solution provided with the equipment and some calibration solutions were prepared in the laboratory. The results for the sampling points are given in the Table 3-2 below in the next section: The pH values recorded during the fieldwork were later discarded due to noticing an error detected in the probe recordings.

Table 3-1: In Situ Water Test Methods

Temperature ˚C	pH	Alkalinity mmol/litre	EC µS/cm	D.Oxygen mg/l	Chloride mg/l
HACH HQ 40D multi probe device	HACH HQ 40D multi parameter probe device	Aquamerck Alkalinity field test kit	HACH HQ 40D multi parameter probe device	HACH HQ 40D multi parameter probe device	Aquamerck Chloride field test kit

Table 3-2: Water Quality Results For In Situ Water Tests In Roxo Catchments, Beja In 2009 September

w 20, w19, w18, a36, a39 are new sample points

Sample point	EW-Cor	NS-Cor	Temp. ˚C	Alkalinity mmol/litre	EC µS/cm	D.Oxygen mg/l	Chloride mg/l
A07	595334	4208084	26.5	6.2	543	8.74	36
A16	583835	4195981	30.2	4.3	1454	6.69	352
A19	580863	4198543	27.8	3.0	1392	7.26	340
A22	593275	4207855	21.4	5.3	722	7.08	36
A23	591530	4205136	21.4	7.3	1114	6.50	130
A24	590483	4203625	21.9	8.9	1614	8.60	274
A25	590255	4202940	25.2	8.3	1446	7.51	224
A26	584458	4207448	19.1	8.2	1032	5.27	90
A27	585011	4200365	28.3	4.3	1452	8.47	380
A28	585565	4193824	23.6	4.4	1570	7.05	360
A29	585748	4189147	27.8	3.9	3300	7.10	978
A31	584832	4198656	30.4	2.8	1469	9.58	360
A33	578416	4187026	26.5	4.3	1603	12.04	390
A36	581852	4198094	29.7	4.0	1398	7.50	350
A39	582399	4200017	26.7	3.4	1437	7.47	368
W08	595336	4208581	20.9	5.3	751	5.52	34
W09	592151	4206624	24.4	4.3	633	8.80	40
W13	595291	4207047	20.8	4.8	798	5.26	26
W14	592116	4206212	21.6	6.3	811	6.35	52
W16	590491	4203631	26.6	2.2	960	8.39	120
W17	574392	4187673	22.1	3.6	1060	4.50	210
W18	598861	4207734	23.6	9.8	1956	7.96	566
W19	586337	4192261	23.1	2.7	3020	4.99	870
W20	585854	4199341	21.1	5.0	2.25	6.10	592

3.5.2. Laboratory Analysis

Water samples from the field were analysed in the ITC laboratory for cations and anions.The cations, Calcium, Potassium, sodium, Magnesium, Iron, Aluminium, Manganese and Silica were analysed using the Inductive Coupled Plasma (ICP –OES) Varian Liberty II instrument. The anions were analysed with a HACH spectrometer. The anions analysed are listed in the Table 3-3 below together with the test methods employed from procedures (Dost, 2006) on water quality sampling and testing field guide. The results of the particular analyses performed on the water samples are shown in Appendix 8

Table 3-3: Test Methods Used In the ITC Laboratory for Anions

Parameter	Method
PO_4^{3-}	PhosVer3 Method Test tube procedure ,programme 535
SO_4^{2-}	Sulphate (0-70mg/l), SulfaVer4Sulfate Powder Pillows, programme 680
NO_3^{1-}	Nitrate High Range (0-30mg/l), Nita ver5Nitrate reagent Pillow, programme 355
NO_2^{1-}	Nitrite Low range(LR), NitriVer3Nitrite powder Pillows, programme 371
NH_3	Salicylate method (0-50mg/l) programme 343

It is also possible to determine the type of the Roxo Reservoir catchment water from these analytical results using Hounslow's classification in AQUACHEM (Hounslow, 1995) in form of a piper plot Figure 3-1.

The water in the Roxo catchment according to Hounslow's classification (Hounslow, 1995) is temporary hard in the wells and saline in the Roxo reservoir. The high level of ions of different elements is consistent with the geology of the area and can be pointed to the metamorphic rocks within the area. Possibly the other contribution are from the calcareous rock formation and their reactions with the water which is not major component of this study.

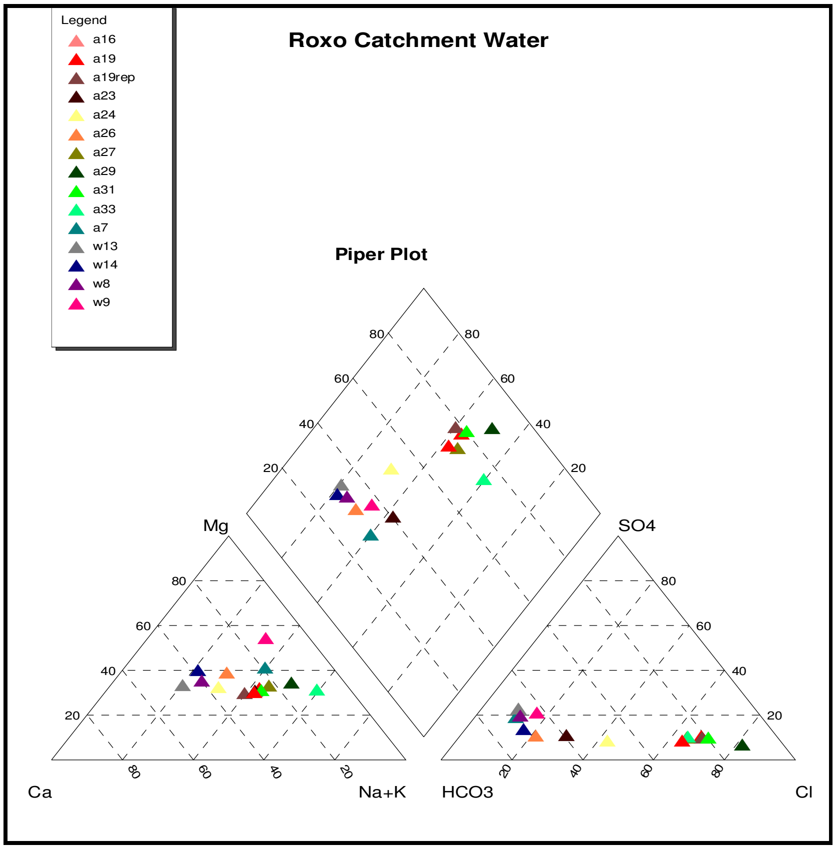

Figure 3-1: Piper Plot of Roxo Catchment water showing the water types

3.5.3. Water quality data reliability checks

3.5.3.1. Chloride versus Electrical Conductivity

As part of the quality check for all the water samples taken, the sodium and chloride analysed against electrical conductivity were checked and shown in figure Figure 3-2. The principle explored in this is the ability of water to conduct electricity due to the presence of ions in it such as sodium (Na^{+}), chloride (Cl^{-}), (Ca^{+2}), (K^{+}), (Mg^{+2}), (SO_4^{-2}) and carbonate (CO_3^{-2}) and bicarbonate (HCO_3^{-1}). Chloride and Sodium were taken in this analysis alongside EC.

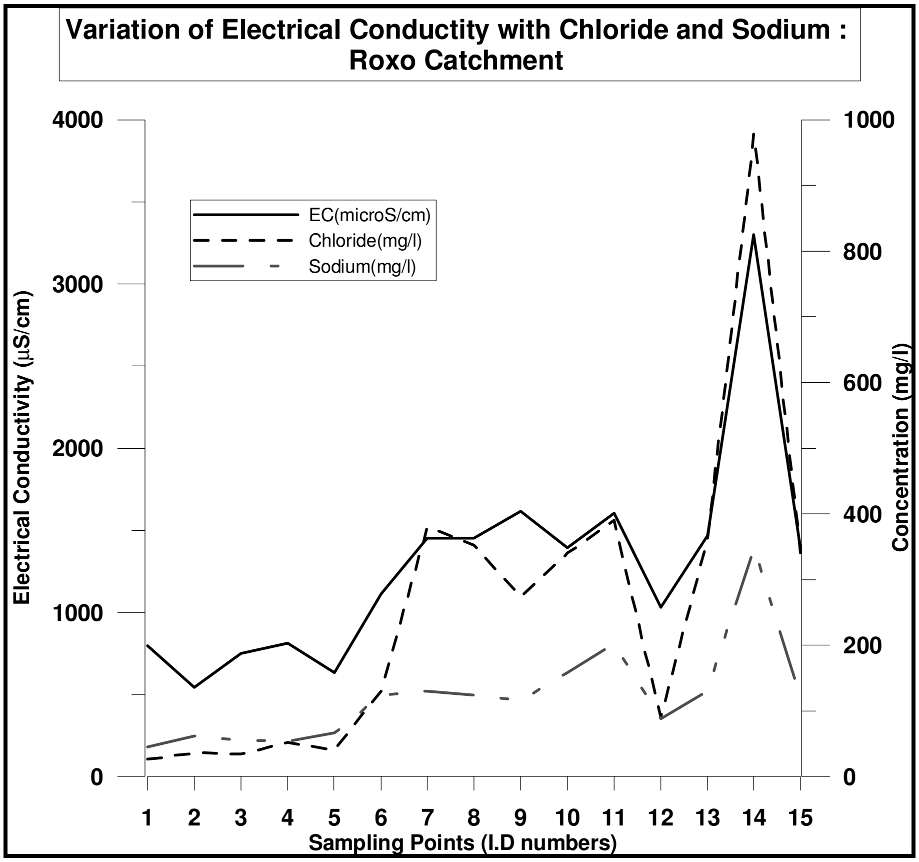

Figure 3-2: Roxo Water samples, Chloride, Sodium variations comparisons with EC (Electrical Conductivity variations), September 2009

The results show a positive correlation between the ions and EC variations. This certifies that the methods used for the analysis and the results obtained are reliable.

3.5.3.2. Cation and Anion balance

Cation- anions balance checks were performed and are recorded in Table 3-4 below. The analysed cation and anions are not an exhaustive list of all minor components as some tests were omitted. Only the most probable anions and cations were determined, and this could account for the failures of some balances by very small margin.

Table 3-4: Cation- Anions Balance Check for Roxo Catchment Water

Sample Point	Cation - Anion Balance	Remark
A16	7.88	Fail
A19	-8.23	Fail
A19(rep.sample)	1.38	Pass
A23	-3.17	Pass
A24	4.43	Pass
A26	-7.25	Fail
A27	12.09	Fail
A29	4.55	Pass
A31	3.56	Pass
A33	6.38	Fail
A7	12.87	Fail
W13	-15.06	Fail
W14	-9.91	Fail
W8	-11.17	Fail
W9	-14.65	Fail

3.6. Numerical water quality modeling analysis

A DUFLOW model prototype (Vithanage, 2009) is used. The numerical model RAM outputs were analysed for the determination of the source using statistical methods such as averaging and summation and getting the percentage proportions of each of the contributing catchments that discharges into the stream network form the RAM areas. This was done in time (over two seasons) and space (different subcatchments). The procedure for the analysis of the RAM modelling results is illustrated in the diagram Figure 3-3.

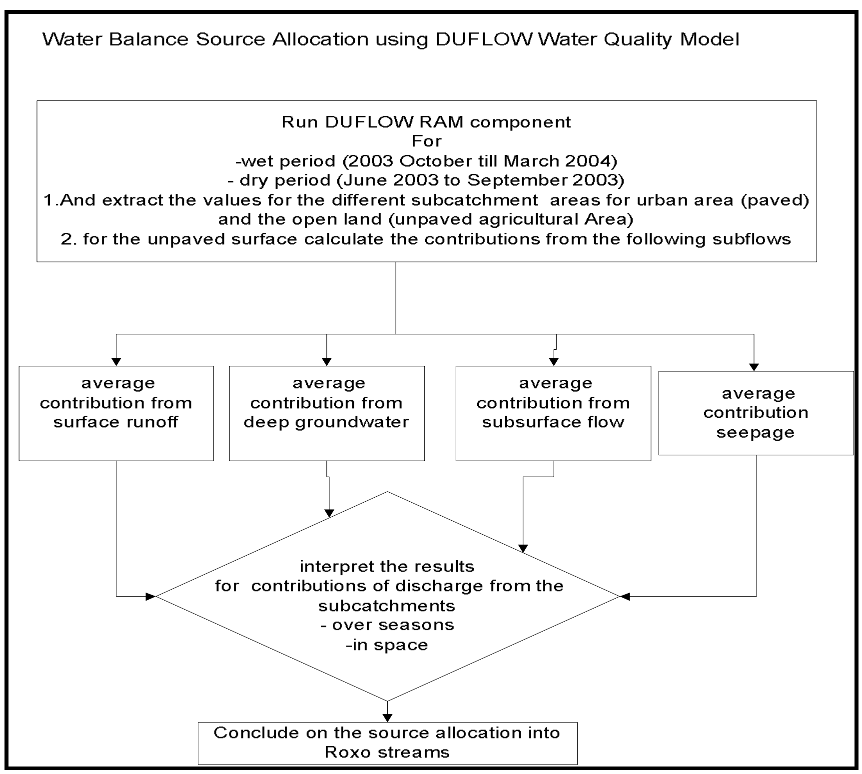

Figure 3-3: DUFLOW water source allocation determination data analyses methods

3.7. Stable Water Isotope Data

Water samples taken in the field (see section on water sampling protocol) for the analysis of stable water isotope (D and $^{18}0$) were analysed at the Vienna Isotope Laboratory using standard methods and the results were reported back to ITC. The results in Table X Appendix 7 were reported in the per mile deviation from the VSMOW (Craig, 1961) as explained in the literature review of its derivations.

Three seasons under analysis are October 2008, the April 2009 and September 2009 fieldwork campaigns. Appendix 2, Figure XVI of the isotope data distribution have been made for better visualisation and comparison on the variation in distribution of the available isotopes data collection within the Roxo reservoir catchment. Isotope data distribution for the periods under study is important in understanding some of the hydrological processes in the whole catchment.

In the month of October 2008 there were fewer (sampling points confined to the Pisoes subcatchment) established and monitored for the water isotope study. Most of the water sampled was in the major stream system running more or less from Beja past Pisoes to the reservoir. There were no wells sampled in that particular sampling season. The data is limited to the analyses of stream hydrological processes in the main perennial stream system.

In the seasons sampled for in April, 2009 and September 2009, the sampling was done on more sampling points covering the whole Roxo catchment area. Since wells, reservoir and streams were sampled. This data is useful in the analyses of hydrological processes in ground and surface water at the whole catchment level.

3.8. Global Network for Isotopes in Precipitation (GNIP) data

Precipitation isotope data is useful in the determination of the Local meteoric water line. The GNIP database recorded by WMO (World Meteorological Organisation) and the IAEA (International Atomic Energy Agency) from worldwide survey campaign on Hydrogen and Oxygen isotopes in precipitation is utilised. The distribution of the meteorological stations participating in this is shown in Figure 3-4 below. The database for the programme that was to determine temporal and spatial variations of environmental isotopes in precipitation is managed by the Isotope Hydrology Section of IAEA. This information was aimed to provide basic isotope data useful for determining framework for use in hydrological investigations within the scope of water resources inventory, planning and development. Global Monthly data from 1961 to 1999 can be obtained from the ISOHIS-WISER (Water Isotope System for Data Analysis, Visualization, and Electronic Retrieval-WISER).

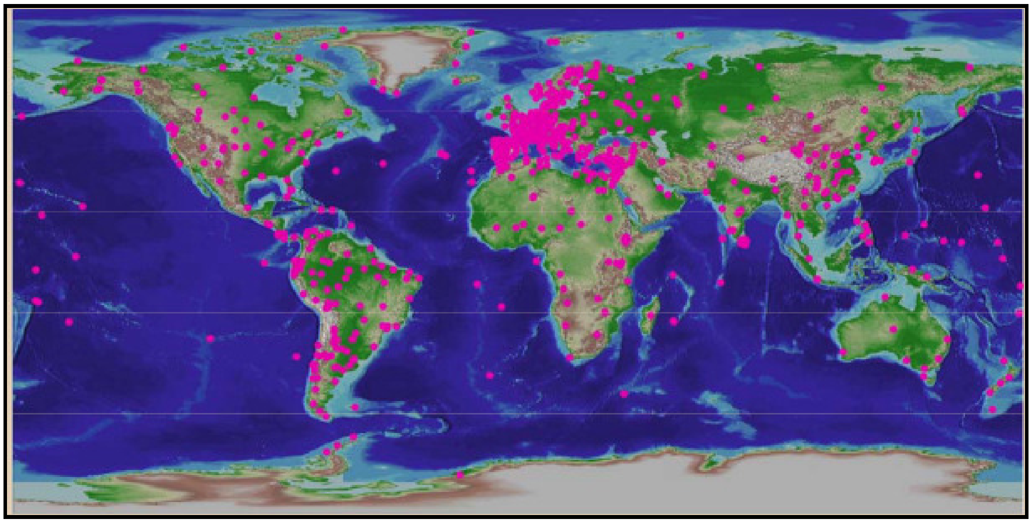

Figure 3-4: Geographic distribution of the meteorological stations belonging to the IAEA/ WMO Global Network of Isotopes in Precipitation: (IAEA, 2006(a))

The data is a composite of monthly rainfall from all the participating stations. Of particular importance in this work is the Beja station. This station (Beja site number: 0856200, Portugal, 38° 0' 36" / -7° 31' 12" / at elevation of 246m) is also available on the GNIP (Global Network for Isotopes in Precipitation) database. This data is for monthly precipitation and is available for the period of 1988 January till 1991 December. Some of the months where there was no precipitation have of course no data (22 records of the 48 possible are available) thus resulting in approximately 50% of the records being available.

The Deuterium and the Oxygen-18 are measured by mass spectrometer method as ratios of deuterium/hydrogen and oxygen (^{18}O over ^{16}O). These are expressed as per mille deviation from the standard (Vienna Standard Mean Ocean Water- VSMOW). The data that was entered in the database has a precision of ± 0.1 per mil for the oxygen-18 and ± 1 per mil for the Deuterium. Before the data was taken into the database obvious errors such as those that resulted form the sampling procedures were eliminated and it underwent constant revision and corrections whenever new information was received form the participating laboratories. (IAEA, 2006)

3.9. Isotope Data analysis methods

The following diagram Figure 3-5 summarises the isotope data analysis that was performed on collected data

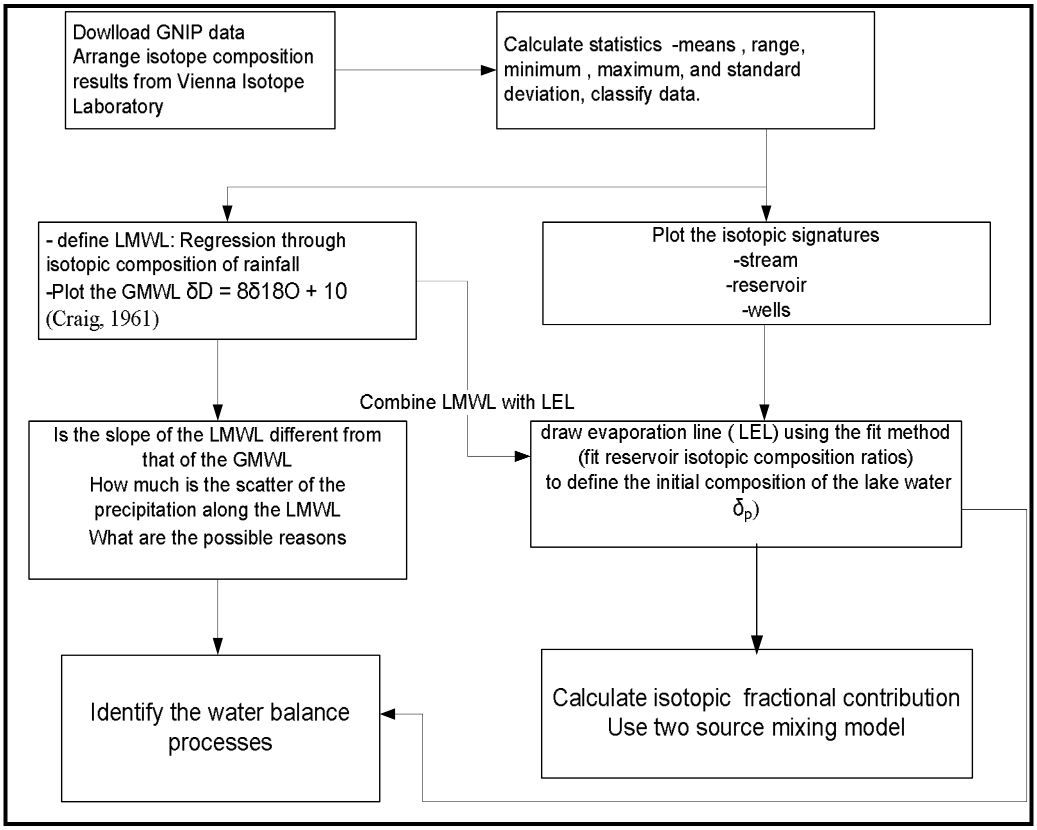

Figure 3-5: Isotope based Water source determination Procedure

The analysis is in 3 phases which can be deduced from the figure above and explained here;

Initially an isotopic study framework was developed by determining the Global meteoric water line and a local meteoric water line. The deviation of the LMWL from the global meteoric water line was analysed and interpreted. To determine the LMWL, least square regression line of the GNIP rainfall data was plotted. Most of the further analyses were done using information obtained from literature and recognising processes precipitation is subjected to. The LEL based framework is also used in the evaluation of processes

Then the spatial and temporal distribution of the isotopes within the Roxo reservoir catchments and between surface, ground and reservoir water were analysed. These were analysed using statistical and graphical software such as Microsoft Excel, Grapher, SPSS 16.0 and Arc GIS 9.3. Results were presented in visual aids such as Inverse Distance Weighted (IDW) interpolation maps graphs, box and whisker plots , descriptive statistics in addition to there GIS systems were utilised. The inverse distance weighted interpolation assumes that the interpolating surface is most affected by nearby points than it is with distant points. The Kruskal Wallis non parametric is the descriptive statistic test method used for testing the differences between median of non parametric samples was also performed to verify the differences in the distribution of the isotopic composition.

The fractional contributions of the water cycle components into the reservoir and the fluxes in the catchment water balance were evaluated using the sampled stable isotope composition data. It is important to note that during the fieldwork period, it was not possible to take precipitation samples for these months as it did not rain as it was the dry season. As such it was not possible to have an indication of the inflow or initial isotopic composition. The intersection of the precipitation line (LMWL) and evaporation line (LEL), can be used to estimate the mean composition of inflow water into the reservoir (Dincer, 1968). It is also taken as mean isotopic composition of local precipitation (δ_p) composition of the inflow (Gibson and Edwards, 2002),and this derivation is indicated in the Figure 3-6 below.

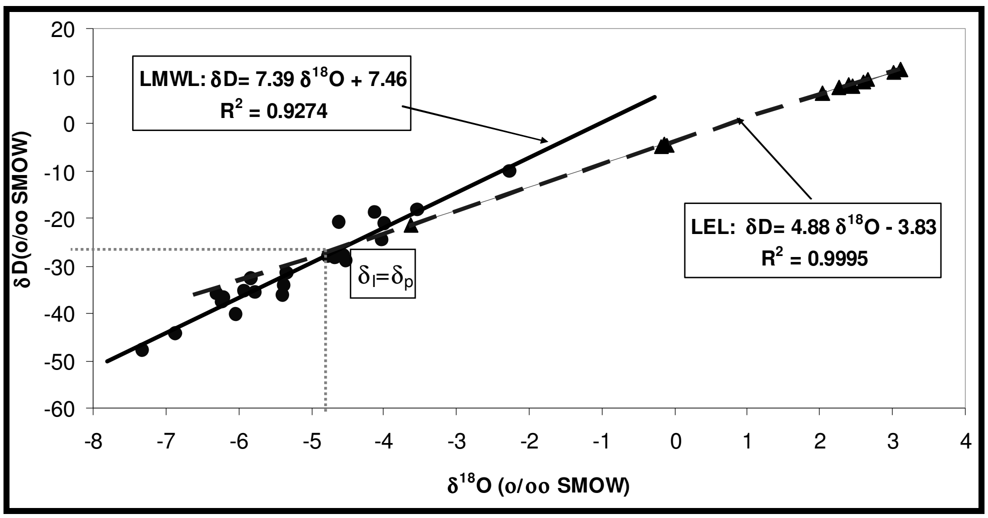

Figure 3-6: Determination of Mean Isotopic Composition Using the Intersection Method(Gibson and Edwards, 2002) . The LEL defined from the Reservoir isotopic composition for the whole study period (September 2008-september 2009)

The (δ_p) composition is -4.5‰ $\delta^{18}O$ and -26.0‰ δD and this value is used in the mixing model.

A two component mixing model is used to analyse the source allocation within the Roxo catchment to the Reservoir and streams. This model assumes that two isotopically different water sources are incorporated into sample component of the water. This mixing computation is conceptually visualised as in Figure 3-7 below. As water from any part of the cycle *x* or *y* into a target sample (s), constitutes a certain proportion in the mixture (z or 1-z), to total of 100% in the sample.

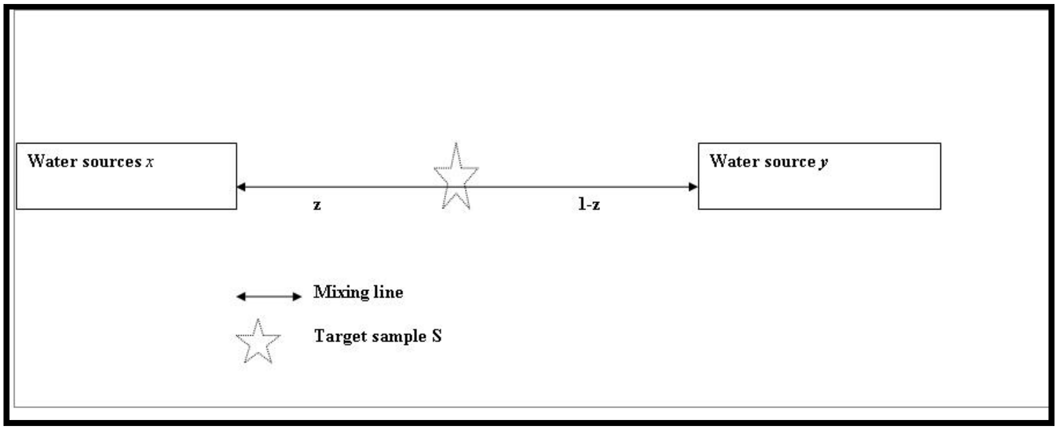

Figure 3-7: The conceptual illustration for the mixing model used in the source allocation from isotope data.

This simple box mixing model adopted (Arusei et al., 2003; Meredith et al., 2009; Ojiambo et al., 2001; Wilcox et al., 2004) can be represented if the following equations with the terms explained above

$$z + (1 - z) = 1$$

Equation 10

$$z(\delta^{18}O_y) + (1 - z)\delta^{18}O_x = \delta^{18}O_s$$

Equation 11

To solve for these equations 10 and 11 the equation becomes similar to Equation 1 of Meredith (2009)

$$z = \frac{(\delta^{18}O_s - \delta^{18}O_x)}{(\delta^{18}O_y - \delta^{18}O_x)}$$

Equation 12

In which z is fraction of y in Sample (s)

This equation is applicable to both Deuterium and the Oxygen 18.

4. Stable Water Isotopes characterisation and source allocation

4.1. Stable Water Isotope results and Discussion

Generally the Oxygen -18 composition ranges form 10.23‰ to -3.65‰ and the Deuterium ranges from 36.60‰ to -24.80‰ for the entire catchment within the all three sampling periods. The summary of the results is shown in the table in Appendix 7 for each season.

The Kruskal Wallis non parametric test for testing the differences between median of non parametric samples was also performed to verify the differences in the distribution of the isotopic composition. These results are shown in Appendix 3. For the streams; the p value is greater than 0.05 for both isotopes $\delta^{18}O$ and δD thus 0.658 and 0.907 respectively. This indicates that there are significant variations between the seasons in the stream samples. The same applies for the wells where the p for the $\delta^{18}O$ and δD are greater then 0.05; 0.186 and 0.09 respectively. However for the reservoir there was not enough evidence to show significant differences between the samples between the three seasons. This is indicated in the statistical result of p being less than 0.05: 0.01for both $\delta^{18}O$.

As shown in Figure 3-5 the order of the analysis of the isotopic data to identify the water balance processes and the determination of source contributions from the various hydrological processes is followed.

4.2. The δ^2H- $\delta^{18}O$ Isotope framework

4.2.1. GMWL and the LMWL

As described before, the GMWL, $\delta D = 8\delta^{18}O + 10$ (Craig, 1961) which gives the description of global fresh water oxygen 18 and deuterium relations, is compared with the LMWL defined from regression of monthly precipitation isotope data of a particular locality. The graph in Figure 4-1 below shows the calculated LMWL $\delta D = 7.26\delta^{18}O + 6.3$ ($\delta D = (7.26 \pm 1.2)\ \delta^{18}O + (6.3\ \pm 9.1)$) for Roxo catchment using Beja station precipitation data collected from 1988-1991(IAEA, 2006). The LMWL of slope 7.2 closely agrees with that defined for the same region but from a larger database 1988 -2001 from ITN (Paralta et al., 2006) $\delta D = 7.67\delta^{18}O + 8.93$ and that of (Carreira et al., 2005) $\delta D = (7.67 \pm 0.44)\delta^{18}O + (8.93 \pm 2.3)$. Slope close to seven was also consistent for a study in Algiers, of $\delta D = 7.15\delta^{18}O + 7.92$ also correlated to be characteristic of rains influenced by the southern Mediterranean sea (Saighi, 2005).

The slope of the precipitation isotopic composition (7.26) in the Roxo catchment samples is less than that of the GMWL (8). The variations in the precipitation data are indicated by the standard deviation 1.19 ‰$\delta^{18}O$ and 9.1‰ $\delta\ ^{2}H$ around the arithmetic mean. Also from box whisker plot of precipitation data Appendix 7 only depicts slight variation in the data due to the closeness of the upper and the lower quartile to the median. The ^{18}O ranges form -2.27 ‰ to -7.31‰ and the Deuterium ranges from -10.1‰ to -47.7‰ in the precipitation data.

A scatter of the precipitation isotopic composition around the LMWL, which predominantly fall to the right of the LMWL, is observed. This can also be attributed to the differences in the source and isotopic composition of rain forming clouds and the occurring partial evaporation. The variation in clouds could have emanated from the variation in the condensation temperatures as well as the compositions of the mass vapours of the precipitation events. Seasonal fluctuations that are observed as the smallest deviation when the plotted as LMWL against the GMWL can be attributed to variations in the vapour source as well as evaporation to which light storms raindrops are subjected as they pass the atmosphere (Araguás-Araguás et al., 2000). This is so since the data was collected during the rainy months over a four year's period resulting in the slightly varying conditions in the source area of the precipitation. The deviation of LMWL from GMWL is a confirmatory observation since such a behaviour of the precipitation composition has been commonly observed in similar arid to semi arid regions (Meredith et al., 2009).

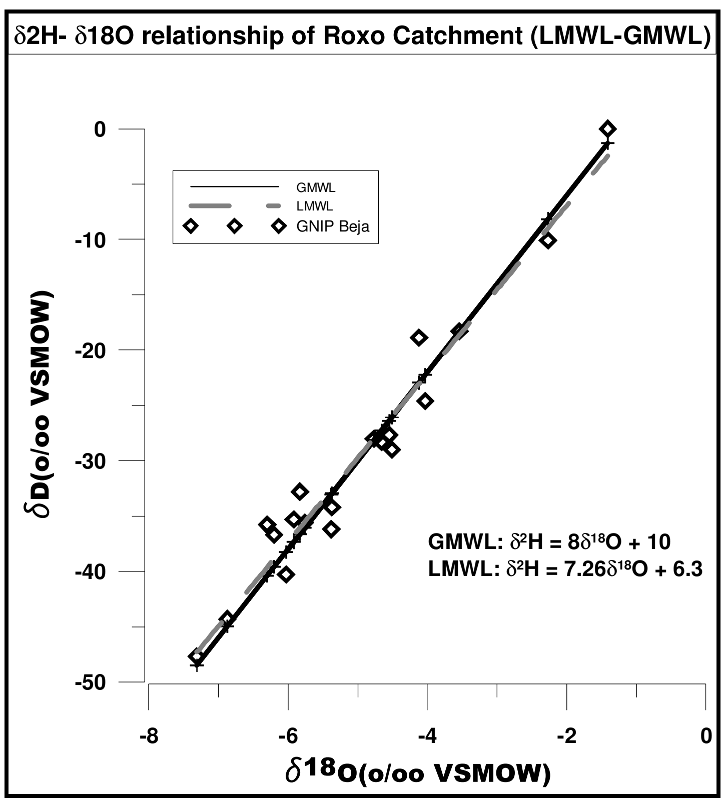

Figure 4-1: Predicted LMWL Roxo catchment from Beja station @(IAEA, 2006) in relation to a fitted GMWL

The GMWL was defined from the one by Craig (1961) and the LMWL was defined from the nearest WMO/IAEA station for GNIP database which is the Beja station Monthly Data from *the (BEJA site number :0856200, Portugal, 38° 0' 36" / -7° 31' 12" / 246m) from 1988 January till 1991 December*

The wet season in Beja is in the winter months as noted before. Therefore the precipitation could be expected to plot close or on the GMWL justifying the LMWL ranges values falling within the 95% confidence interval of GMWL. Isotopic enrichment of precipitation during these periods is abridged by the prevailing low temperatures experienced during winter rainfall events, Figure 1-2. The highest evapotranspiration is recorded in the September (dry months) thus not within the rainy months. The fluctuating variations in isotope composition of the precipitation called the "amount effect" (Ingraham, 1998) are presented in Figure 4-2. The "amount effect" is described by the tendency of water collected during smaller rainstorms to have higher isotopic enrichment than that collected during larger storms.

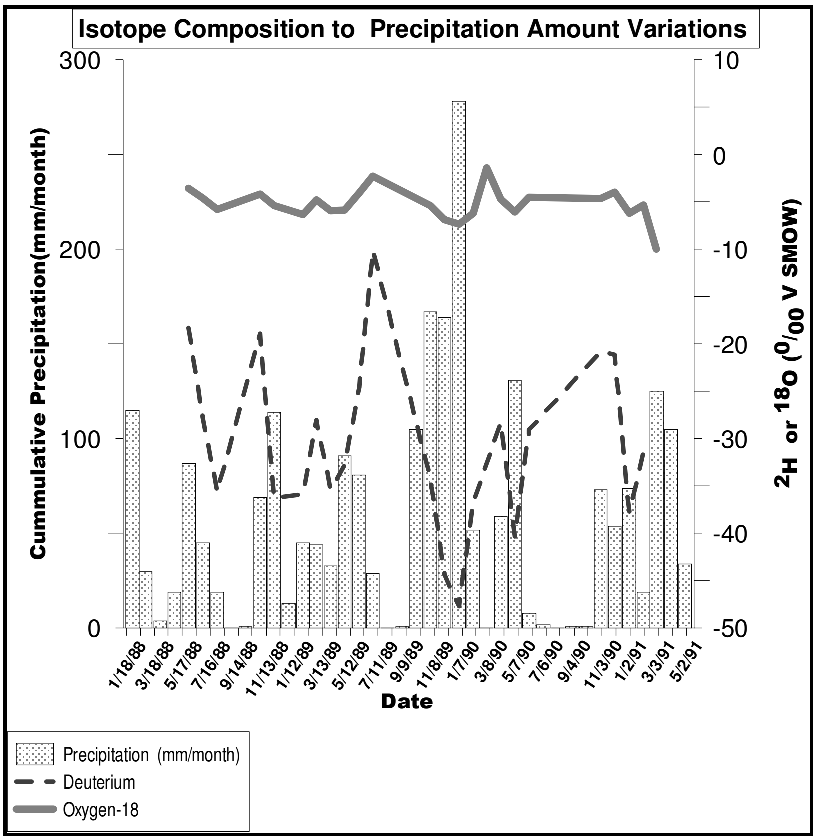

Figure 4-2: Isotopic composition of precipitation with respect to the precipitation amounts @(IAEA, 2006) at the Beja weather station.

Generally the cold months are associated with the heavy rain hence the depleted isotopic compositions. For warm rainy months, the precipitation isotopic composition is more enriched.

4.2.2. Distribution in Roxo Reservoir catchment

The isotopic compositions of waters in the Roxo catchment are tabulated in Appendix 7. In addition to this the spatial distribution in isotopic signatures in surface waters is illustrated in the IWD (inverse weighted distance interpolation maps) , Appendix 2, Figure XVI.

Isotopic framework utilised for the determination of the water balance hydrological processes and qualitative interpretation of sources revolves around the interpretation of Local Evaporation Line (LEL) (Wolfe et al., 2007). In this study, the reservoir isotope water compositions data is used to define a LEL for each of the seasons. Figure 4-3 below shows the LEL based isotopic framework for each of the two seasons the wet (April) and dry (September) under study. The plot of the data points above the LEL indicates rainfall events during the wet season (Wolfe et al., 2007). For understanding the isotopic influences and variations it is crucial to keep in mind the weather conditions as these have a huge bearing on isotopic response Figure 4-4.

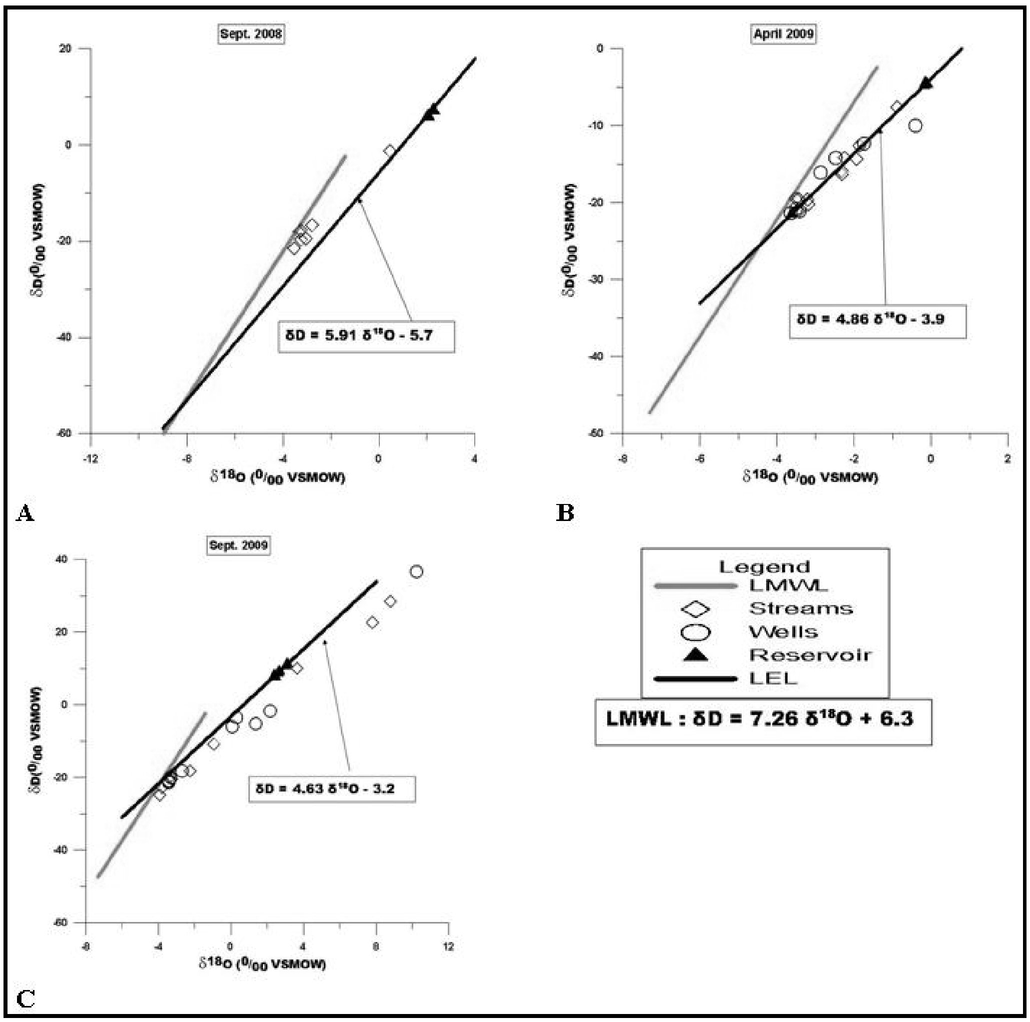

Figure 4-3: Bivariate plot of the distribution of Isotope ratios in the Roxo Reservoir Catchment water balance components (surface, wells and reservoir) (a) September 2009 dry season and (b) April 2009 ,wet season and (c) September 2009, dry season.

The LEL is defined by the equation in each graph and derived from the Reservoir isotopic composition in each case. This is compared to the LMWL see legend.

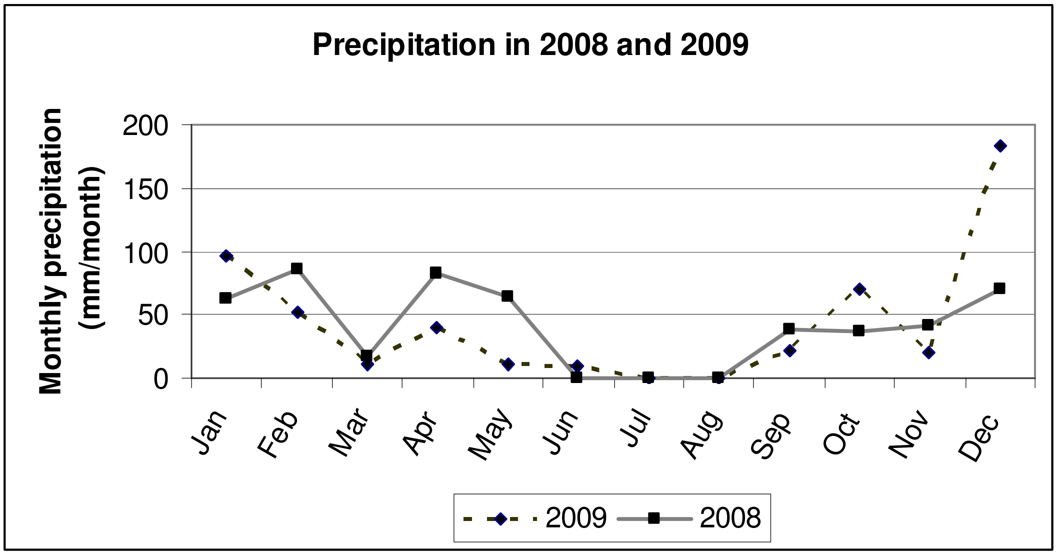

Figure 4-4: Precipitation Variation within the Sampling Years of Roxo Reservoir Catchment Isotope Data

The values plotted on this graph result from the monthly averages of precipitation data from COTR (www.cotr.pt) to show the general trend on the precipitation variations that are necessary to describe isotopic variation in some instances.

The average isotopic compositions of the reservoir in the September 2008, April 2009 and September 2009 were characterized to be 6.95, -8.82 and 9.28‰ δD and 2.15, -1.02 and 2.70 ‰ $\delta^{18}O$ respectively. Due to the increased residence time during which the reservoir water is exposed to atmospheric motion vectors and therefore increased evaporation (Diefendorf and Patterson, 2005; Gibson et al., 2002), this gives the reservoirs higher isotopic compositions. Reversal in the isotopic enrichment in rainy months and dry months as in the figure A,B,C agrees with studies carried out in several areas (Gibson, 2002) and theory (Dincer, 1968), rain inflow into the reservoir results in dilution. The average isotopic composition of the reservoir water in the dry season (September) is about the same magnitude for the 2009 and the 2008 dry seasons. The September sampling is affected by some unexpected rainfall during the fieldwork campaign as it generally begins raining at the end of month, these weather conditions can be read from Figure 4-4. In the wet season all the water sampled almost fall on the same LEL Line representing similar compositions. An overlap in the isotopic compositions for some of the stream and groundwater sampling points Figure 4-3(b,c) displays the possibility of similar source (Liu et al., 2008) for this water or an interaction (hydraulic connection) between them. This interaction is possibly because of mixing in some of the stream water with groundwater sources that plot close together. This can also indicate that the water that is recharged into groundwater undergoes evaporation before recharge.

The slope of the LEL for the Roxo reservoir varies from 4.6-5.9 which is consistent with the LEL is in other semi-arid regions as majority of Ethiopian reservoirs which fell between 5.2 and 6.4 (Kebede et al., 2009). These are reasonable slopes plotted off the isotope composition as these belong to similar dry climatic environments since in the Canadian streams and reservoirs different results are reported, (Gibson et al., 2002).

All the isotope composition points plot to the right of the LMWL indicating that the water is subjected to substantial amounts of evaporation. Some of the streams and wells of 2008 September plot away from the LEL yet closer to the LMWL, thus indicating some mixing with isotopically depleted water. However for the period of the wet season wells have the lowest slope due to the time it takes for the isotopically depleted precipitation dilution effects to dilute the groundwater.

Majority of the wells do fall on the same isotopic depletion line to the right of the LMWL as the streams and this indicates that the water was subjected to some evaporation processes before ground water recharge. It could also indicate that the river water is being kept running by the inflow of mainly ground water in some areas especially for the April season, Figure 4-3(b). During the rainy season there is more intermixing of the water thus making it difficult to differentiate between the different water sources as all plot along the LEL

The A31 sampling point on one of Roxo Reservoir's side streams (Roxo arm) collected in the wet season (April) 2009 presents an outlier in the isotopic results. When this sampling point is excluded, the averages of δ^2H and the $\delta\ ^{18}O$ were -4.6 ‰ and -0.15 ‰ respectively where n =3. The well water sample W18 is more of an evaporative pond in a very dry area. Due to the dryness in this southern part of the basin the isotopic composition of water is here more enriched.

During the dry months the southern catchment and the reservoir have the most enriched composition. The sampling area around A23, 24, 22, 25 in the north are within the same isotopic range. In the wet season (April sampling), there is no significant variation between the isotopic composition of the stream at points A7, A22, and in the composition of the wells at W8 and W13, see map of sampling points for their positions; Appendix 1 and the IWD interpolation maps , Appendix 2, Figure XVI. This could be as a result of the ground and surface waters intermixing but most likely that it's a result of both having an input of precipitation in April (Figure 4-4) towards the end of the wet season. W9 and W16 are water sampling ponds fed by groundwater in the northern part of the catchment, in the Pisoes sub-catchment, and are more isotopic enriched than the other closed groundwater sources (wells). The closed wells in the Outeiro subcatchment (northern part) that includes the Pisoes sub-catchment are more isotopically depleted than those in the southern subcatchments especially W20 and W17.

Water composition at A28 of water fed by small streams and reservoirs in the south of the catchment, has isotopically enriched water which highlights evaporation contribution, as already explained earlier. The differences in the north and southern subcatchments wells and streams isotope compositions can be attributed to the differences in geology of the area described in Figure XIV, Appendix 9 Where there is an evident fault in the Beja area and the Gabbros of Beja aquifers (Paralta et al., 2006; Paralta and Oliveira, 2005). This escarpment is assumed to have yields of 5 l/sec to 36 l/sec (Duque, 1997). In the south at the points A28 also represented peculiar characteristics because of the geology of the area as it is crossed by a shallow fault see Appendix 9.

4.3. Water source allocation

In the dry months the Pisoes stream waters are depleted in isotopic compositions although they would be expected to be enriched because of prevailing dry conditions. The presence of depleted isotope values even in low flow of the dryland of the Pisoes sub-catchment (observed in fieldwork) can be attributed to the isotopically depleted groundwater and bank storage water influx along the river (Meredith et al., 2009). This suggests that there is some groundwater inflow from the nearby identified WNW-ENE fault escarpment (Paralta et al., 2003) Appendix 9 that seeps into the streams, more so around the A23, A24, and A25 area. These areas were found to have flowing perennial streams. Paralta et al., 2005, mentioned that gabbro-dioritic shallow aquifer located in the north part of the catchment, one of the most productive formations in South Portugal have recharges between 10 % and 20 % of average annual rainfall (500 mm/yr) according to recent recharge models, and occurs mainly between January and March/April. However this same discharge is reported to derive directly from precipitation (Duque, 1997), hence the more depleted signature.

It is also noted that there is an anomaly in the composition of the mid section points of the Pisoes subcatchment as in the dry season, when enrichment is expected because of dry conditions, they are actually more depleted. For example sample point A23 in the April season, has -12.6‰ and -1.86‰ for δD and $\delta^{18}O$ respectively yet in the drier September season, it is -20.45‰ and -3.25‰ respectively. Probably this is due to delay period from the shallow aquifer discharge mentioned above. At sampling point A31 the earlier on explained anomaly can be attributed to the presence of the fault line through this point.

This groundwater escarpment discharge can be estimated to have the composition as that of the average of the deep wells in the northern part of the catchment. The average composition calculated is shown in Table 4-1 below

Table 4-1: Average escarpment contribution of the deep groundwater assumed to be causing dilutions in the Pisoes catchment.

	d^2H [‰]	$d^{18}O$ [‰]	d [‰]
2009 Sept	-21.14	-3.41	6.10
2009 April	-17.93	-2.93	5.55

Water source allocation is quantitatively evaluated by the partitioning of the various fluxes in terms of their fractional contributions (% of volume). The two source isotope mixing computation is performed using the Equation 12 adopted from Meredith (2009) as given below. The results of the analysis are shown in the table below. The average precipitation value used as input into the catchment is derived from the intersection line of the LMWL Figure 3-6 and the general LEL, noted to be is -4.5‰ $\delta^{18}O$ and -26.0‰ δD

$$f = \frac{Cs - Crw}{Cgw - Crw} \times 100$$

Cs mixed water is taken to be the average isotope concentration in the reservoir and *Crw* is taken as value of the river water or the groundwater or the precipitation water whereas Cgw is the average for the source that we suspect to be influencing

Several scenarios are used to determine the contribution to the stream water and reservoir water from under ground, precipitation and the deep groundwater from escarpment, the results of which are shown in Table 4-2 below. The average contributions are utilised in the analysis.

Table 4-2: Fractional contribution (f) in percentage (%) of Groundwater and escarpment to the Northern streams and that of Groundwater, escarpment flow and surface water to the Roxo Reservoir

	Sample/direction of contribution	f(GW)	f(ppt)	f(escarpment)	f(streams)
Sept 09	**Streams**				
	Northern	60	40		
	Northern	18		82	
	Reservoir				
	South	55			45
	north	-			-
	north	22		78	
	south		34		66
	When the catchments are separated				
		f(GW1)	**f(GW2)**	**f(ppt)**	**streams**
	sample 24/25		27	73	
	sample 24/25	62		38	
	sample 24/25			25	(w14)75
	a28 (south)	121		-21	
	a28 (south)	42			58
Apr 09	**S streams**	73	27		
	N streams	102	-2		
	N streams	121		-21	
	reservoir				
	south	178			-78
	When the catchments are separated				
		f(GW1)	**f(GW2)**	**f(ppt)**	**surface**
	24/25	-80		180	
	a28 (south)	57		43	
	a28 (south)	-59			159

Notes: ppt refers to precipitation; GW refers to groundwater determined from the wells isotopic signature, GW1 refers to groundwater from the upper pisoes catchment from and GW2 refers to the lower pisoes catchment.

The contribution form the southern sub-catchments from precipitation is about 43% and 57% from groundwater into the discharge stream into the Roxo Reservoir at A28. However, that calculated from the southern catchment into the reservoir, by looking at the "mixed" reservoir signature, is 34% from precipitation, and 66% from the streams. 55% is from groundwater when compared to streams contribution of 45%. However in the wet season, 73% is assumed to come from the groundwater and only 27% direct from precipitation. The average contribution from the groundwater to the northern streams is 39% and about 80% of the water in these streams is estimated to originate from the escarpment sources. Some contributions were negative but negative fractional contributions into the reservoir are not an uncommon thing in the dryland climates. Results of an Australian study (Meredith et al., 2009) highlighted the same problems in which such variations indicate the evaporation processes effects to which the water is subjected.

The effect to the Roxo reservoir was hard to establish because of the very high evaporative effects affecting it. . The strong evaporative effects on the isotopic signatures do not permit some of the sources to be identified in the mixture signature as at times the mixture falls out of range of the samples. This falls outside the scope of the two component mixing model as it was too simplified for the processes within the reservoir as explained in following paragraphs.

Direct Precipitation seems to have less effect in the Roxo Reservoir catchment between 27%-43% into the contributions since that the amount of precipitation is generally low in the Roxo catchment. This can also be attributed to the geology in the area where with the sandstones in the south, and the quartzite derived soils, there is bound to be more infiltration when it rains with less runoff. Most water therefore is from the subsurface and surface sources.

Whilst this simple box model is usable in assessing the general trends in some sections, some problems are still inherent to the model. Such include mixing that could occur across geologic layers in evaporation where an input of rainfall or a more depleted source would increase the influence of the enriched form so as to compensate for the imbalance. And input of isotopically enriched water would shift the higher contribution to the isotopically depleted form. This method shows difficulties within the concept due to the influences of evaporation fluxes and changes not being directly incorporated. Fractional contributions above 100% show that there are other processes that are not incorporated so that the isotopic signatures can give contribution of 1, such processes include fractionation (Phillips et al., 2005). The simplified mixing model does not account for the fractionation factor between the sources, it can therefore be recommended that an apparent fractionation factor (McKechnie et al., 2004) be considered for study to include into the model.

The other setback in the analyses could be the over estimation of the isotopic depletion resulted from the incidental rains that fell outside the rainy season directly in the small streams which happened at the occasion of some of the sample collection in September see rainfall graphs Figure 1-1 and Figure 4-4 . Since there was no direct measurement form the escarpment aquifer discovered to be the Gabbros of Beja referred to before, estimation might not have been fully representative of its composition.

The model can be further adapted to a complex box model (Wilcox et al., 2004) hence to incorporate more processes by the use of the other parameters such as isotopic content of evaporation moisture among the other inputs. Estimation of source contribution form any similar source components may be difficult in their interpretation. The high level of intermixing in addition to challenges mentioned above were also a difficulty factor to be overcome by more sampling periods data to capture variations.

5. Numerical Water Quality modelling and source allocation

5.1. Numerical model data analysis

An insight into the different hydrological process and contributing areas is necessary for the correct description of precipitation and runoff processes in water quality studies. This implies a correct description of runoff and leaching, to complement isotopic study (as control), DUFLOW RAM model‘s applicability to such a study is tested.

The Numerical Model (Duflow), RAM flow and quality model (Vithanage, 2009) were run for various time periods for the wet and dry periods as indicated in Figure 3-3. The adjective-dispersion matter transport routes in the river are then analysed based to allocate the source area both in surface and subsurface in the paved (urban), the unpaved influence (RAM Area-agricultural or other activities). 13 catchments were grouped and those whose results can be compared with isotope study noted RAM area Northeast (4, 5) and southern (12).

5.2. Water source allocation

Important to note is that the partitioning of the water source within Roxo catchment is limited to the surface and the subsurface runoff resulting form precipitation that falls within the catchment. The groundwater (shallow aquifer) component contributions were accounted for using seepage component in every sub basin. The diagram Figure 5-1 below adopted from literature (Kendall and McDonnell, 1998), indicates the important hydrological water flow pathways the RAM component does focus on that are crucial in the analysis leading to a total runoff. The concept to this analysis is that with the evaporation included, the water initially falls to the surface then ends up in the stream through the various methods such as groundwater flow, subsurface flow and the surface flow which to an extent includes the channel and the precipitation.

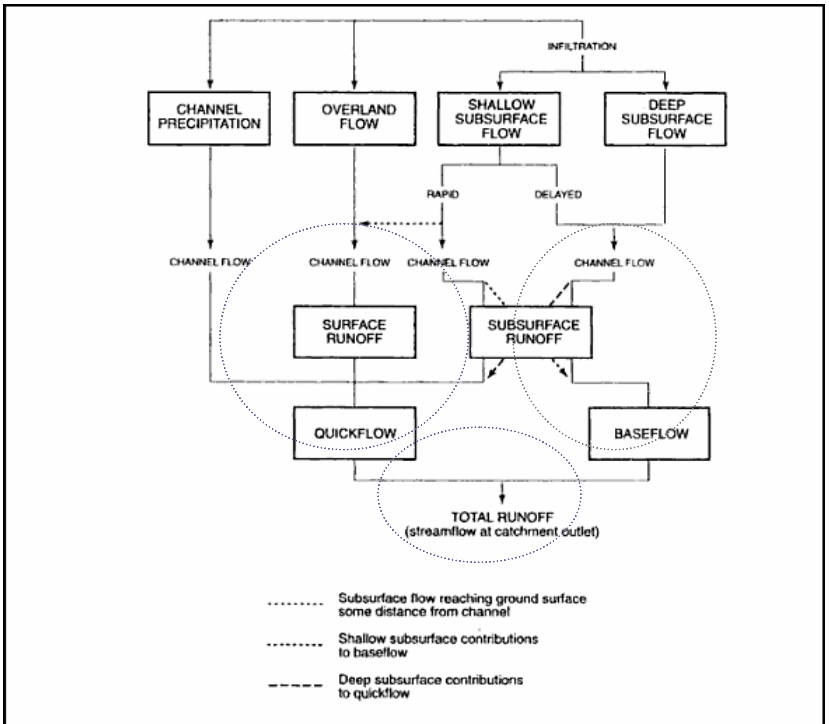

Figure 1.9. Pathways that rainfall and snowmelt may follow to reach the catchment outlet as streamflow (modified after Ward and Robinson, 1990).

Figure 5-1: Pathways of rainfall within and out of a catchment. Figure adopted from (Kendall and McDonnell, 1998).

This figure assists in the understanding of the concepts and terms referred to in the RAM (circled in grey) Model used in this study. These are the quick flow, the delayed flow and the surface runoff.

In the RAM model, paved surface would be the urban residential areas (STOWA, 2004(a)) such as part of the Beja, the unpaved surface areas would be agricultural areas. The unpaved part is of particular importance in that it constitutes the surface runoff after all the infiltration processes have occurred and the groundwater flow. In the northern to north eastern part of the catchment, unpaved surface is under agricultural area yet at the southern region is mostly under forest plantations and range area. The analysis was done for several subcatchments demarcated on the map in Appendix 1 subdivided on the basis of the reservoir arms they supply water to, as highlighted in Table5-1 below. The table below shows the source allocation flow in the Roxo reservoir subcatchments. This analysis is done for the two major distinct seasons of the Roxo catchment which are the wet and the dry season. Dry period was defined for June to September 2003, and the wet period was de fined as from October 15th until 29th of March 2004 in the analyses. This is to get a general behaviour of the water sources and water distribution within the catchment from a modelling point of view.

Table 5-1: Source allocation analyses grouping of subcatchments in the Roxo catchment

Catchment Area	Represented region
6,7,10	North
4,5,9,11	North East
3	East
8	South East
1,2,12	South
13	*Roxo reservoir

* means the source allocation cannot be calculated within the reservoir

The results of the analysis carried out are recorded in the Table 5-2 and Table5-3 below. Several assumptions were considered to be able to make us e of the Ram data. Firstly as mentioned in the prototype development initially a constant inflow from the WWTP of Q = 120.0 l/s, NO3-N = 20mg/l.where with application of F=QxC the Load at WWTP, the load F= 2.4g/litre. These values were based on real measured and documented values. The nitrates are not fully described in this research they were analysed for illustration only.

Table 5-2 Average Flow and nitrate loads from the different source areas in the Roxo catchment during the (a)wet and the (b)dry seasons

(a)

Subcatchment group	Flow Discharge contribution l/sec					Nitrate load contribution g/sec				
	Open water	Paved surface	Unpaved surface	Seepage	Total	Open water	Paved surface	Unpaved surface	Seepage	Total
North	0.0	4.3	187.2	4.4	195.9		0.0	1.4	0.2	1.6
North east	2.5	132.4*	149.3	3.1	165.4	0.0	2.4*	1.1	0.1	3.6
East	0.0	0.0	141.3	3.6	144.9		0.0	1.0	0.1	1.2
South east	0.0	0.0	274.4	6.7	281.1		0.0	2.0	0.3	2.3
South	3.2	0.0	259.3	7.1	267.4	0.0	0.0	1.9	0.3	2.2

(b)

Subcatchment group	Water discharge l/sec					Nitrate loading g/sec				
	Open water	Urban Area	Unpaved area flow	Seepage	Total	Open water	Urban Area	Unpaved area flow	Seepage	Total
North	0.0	0.0	71.4	4.4	75.8		0.0	1.6	0.2	1.8
North east	-8.3	120.0*	49.9	3.1	50.9	0.0	2.4*	1.1	0.1	3.6
East	0.0	0.0	58.3	3.6	61.9		0.0	1.3	0.1	1.5
Southeast	0.0	0.0	108.6	6.7	115.3		0.0	2.5	0.3	2.8
South	-13.6	0.0	114.6	7.1	117.1	0.0	0.0	2.6	0.3	2.9

** North East paved surface includes the Outeiro paved surface Beja city and the Beja Town WWTP flow discharge and nitrate load*

Table 5-3: Source allocation in % contribution to the Roxo reservoir inflow from the various subcatchments during the wet (a) and dry (b) season.

a)

Subcatchment group	Flow Discharge contribution %					Nitrate load contribution %				
	Open water	Paved surface	Unpaved surface	Seepage	Total	Open water	Paved surface	Unpaved surface	Seepage	Total
North	0.0	3.2	18.5	17.7	16.7	0.0	0.1	18.6	17.7	14.4
North east	43.4	96.8*	14.7	12.4	24.3	43.4	99.9*	14.3	12.4	33.2
East	0.0	0.0	13.9	14.57	12.3	0.0	0.0	14.1	14.5	11.0
Southeast	0.0	0.0	27.1	26.9	23.9	0.0	0.0	27.4	26.9	21.2
South	56.6	0.0	25.6	28.4	22.8	56.6	0.0	25.6	28.5	20.1
Total	100	100	100	100	100	100	100	100	100	100

b)

Subcatchment group	Flow Discharge contribution %					Nitrate load contribution %				
	Open water	Paved surface	Unpaved surface	Seepage	Total	Open water	Paved surface	Unpaved surface	Seepage	Total
North	0.0	0.0	17.7	17.7	14.0	0.0	0.0	17.7	17.7	14.5
North east	37.8	100.0*	12.4	12.4	31.6	37.8	100.0*	12.4	12.4	28.5
East	0.0	0.0	14.5	14.5	11.4	0.0	0.0	14.5	14.5	11.8
Southeast	0.0	0.0	27.0	27.0	21.3	0.0	0.0	27.0	27.0	22.0
South	62.2	0.0	28.5	28.5	21.6	62.2	0.0	28.5	28.5	23.2
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

** North East paved surface includes the Outeiro paved surface Beja city and the Beja Town WWTP flow discharge and nitrate load*

From the analysis generally the north eastern catchment that constitutes the Outeiro catchment including the effects of the WWTP contributes a great proportion of the water that discharges onto the Roxo reservoir according to the simulation results analysed above. The north eastern subcatchments in the wet season contribute 24% of the total inflow into the Roxo reservoir from the catchment. In the drier period, the same subcatchments contribute 31% of the total inflow into the Roxo Reservoir, this difference between the dry and the wet season us registered. This can be attributed to the fact that as could be expected, in the dry period, most of the water is noticed in the North eastern subcatchments when the others are more or less dry. Also in the model parameterisations, a discharge had been measured for the Outeiro catchment when none was measured in the southern catchment. The unpaved surface from each of the subcatchments indicates the most contribution as compared to the urban runoff and seepage.

The source allocation was further analysed within the paved surface to determine the percentage of the contribution from the different hydrological system pathways as groundwater, surface water and subsurface flow. A diagram Figure 5-2 below is represented for one of the catchments to illustrate the general trend. This particular trend was identified as it was assumed some parameters were constant over the catchment in the prototype Vithanage

(Vithanage, 2009). Two samples of the data were taken to achieve this that is the Northern and the Southern group of subcatchments.

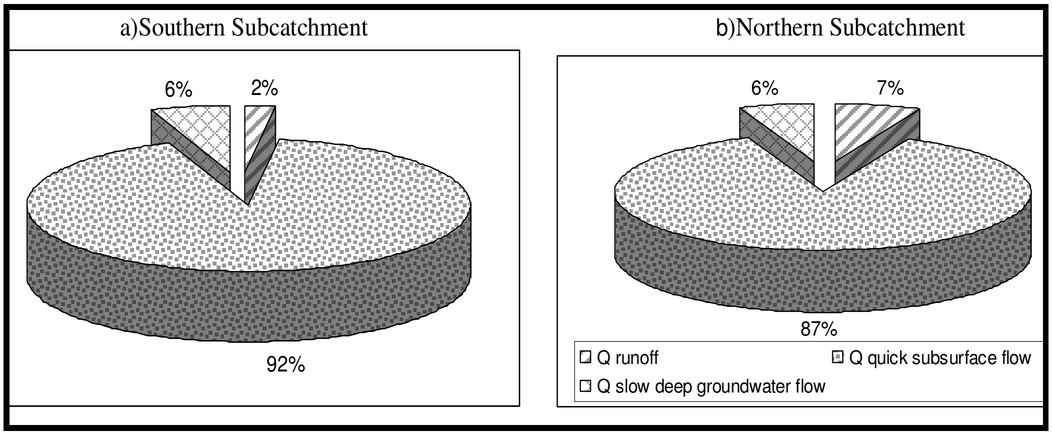

Figure 5-2: Hydrological processes Source Allocation in % in the Southern subcatchments and the North Eastern Catchments for the Wet season

The distribution of the unpaved surface discharge within the subcatchment is based on the DUFLOW RAM model output for the wet season. Checker boxes represent the deep groundwater flow, the diagonal lined indicate surface runoff and the dotted piece represent the quick flow that flows through the shallow subsurface.

The seepage contribution is assumed constant for the whole catchment in the model prototype using sum total, it is therefore ignored in the analysis. The total is taken as the total flow that discharges to the streams after a while and this is taken to be useful in the calculation of the various sources.

With the very low rainfall received generally, for the dry period the main contributing factor in the whole catchment as a whole depends on the groundwater only. This can be attributed to overland runoff in dry season Figure 5-2. The MSG MPE, rainfall amount for the whole catchment show a positive correlation and no significant difference yet rainfall is one of the major driving factors to the results of the RAM for source allocation. The non variability of the precipitation amounts within the catchment makes Ram numerical source allocation determination an intractable approach if the other soil parameters are almost homogeneous.

In the southern part of the Roxo catchment in the area 12 and 2 subcatchments that area mainly dominated by forest and plantations, the contribution due to runoff (2%) is less than in the northern part (7%). This could also be because the water is able to infiltrate more than for the other agricultural areas in the north. The vegetation cover in this area mainly the plantations could have an effect in real life then the model could be assumed to duplicate an element of reality.

Very low rainfall recorded on few days in the dry period hence it would be justifiable that the main contributing factor in the whole catchment as a whole depends on the groundwater only. However the results are more or less similar for the north and the southern catchments. This shows a limitation in the model when used without enough experimental data to further parameterise it. From the analysis of the MSG MPE, the rainfall amount for the whole catchment show a positive correlation and no significant difference between different points, yet rainfall is one of the major driving factors to the results of the RAM for source allocation. The non variability of the precipitation amounts within the catchment makes Ram numerical source allocation determination an intractable approach. As the other soil parameters are almost homogeneous, and the unavailability of data in the southern part of the catchment, this makes the evaluation of the RAM outputs difficult.

The results from the Duflow model have groundwater contribution highlighted to have more influence in the dry (summer) season than in the wet season (winter). Like conclusions and results in other study area, in the summer season in Roxo catchment seepage discharge the same order of magnitude as the summer steamflow discharge. This same conclusion was reiterated in study in Tomales Bay (Oberdorfer et al., 1999). Groundwater is a major component of the catchment freshwater balance in the wet months from analysis of the results.

However the general performance can be estimated by interpreting along side the isotopic data. This is done to check if there is coherence to the general trend in the results from processes derived from the isotopic data in previous chapter. The model however does not show the marked difference between the north and south as shown by the isotopic signatures.

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6. Conclusions and recommendations

Based on isotopic signatures and ratios, the framework for the isotopic study could be defined. Precipitation LMWL is able to show minimal evaporation with LMWL of $\delta D = (7.26 \pm 1.2)\ \delta^{18}O + (6.3 \pm 9.1)$ since precipitation falls in winter season with majority of days with very low evapotranspiration. As indicated in the general LEL of $\delta D = 4.88\delta^{18}O + 3.83$ for all the samples collected for the three seasons, this indicated high evaporation effects

Roxo catchment behaves like two different catchments. The southern part of catchment behaves as expected in arid regions where in dry season there is isotopic enrichment in streams and the opposite is true in the wet season. The northern subcatchment stream water is even more depleted in the dry season. This is attributed to the effects of an influx from the escarpment influx that is much stronger in the summer season where it the stream water depletion through dilution. These areas were observed to be green during the fieldwork surveys and that is where the streams had higher flows than other areas. This highlights to the effects of the geology in the area. The presence of the WNW-ENE escarpment fault that divides the Beja mafic –ultramafic complex and its adjacent Gabbros of Beja aquifer can be attributed to this inflow. This is one of the major water sources that affect the Northern part of the catchment hence its wetter and more depleted than the southern part of the catchment.

The effects on the reservoir and the allocation to the reservoir were not correctly evaluated as evaporation strongly influenced the reservoir signatures and was not accounted for by the simple two component mixing model. To over come this limitation, it might be useful to incorporate a multi-component mixing model at that accounts for fractionation, diffusion into and out of immobile phases and analysis of kinetic effects .These processes are ignored in the model used in this research and to be accounted for requires more samples to be analysed and incorporated.

Thus in the northern part even after determining the source allocation, 80% of the water is estimated to emanate from the escarpment water. The effects of precipitation directly into the reservoir from the southern catchment by looking at the “mixed” reservoir signature, is 34% from precipitation, and 66% from the streams. As evidenced by the analyses in terms of the isotope source allocation for the southern catchment, groundwater contributes a substantial (42-57%) amount of water to the streams and eventually even to the reservoir water balance. However this contribution is not very much noticeable in the Roxo reservoir from the mixing model applied as isotopic signatures of sources are outweighed by the presence of strong evaporation fractionation within the reservoir.

The use of the numerical model is not entirely able to determine the different contributions between the catchments for the various subcatchments because of the generalisations assumed for some parameters. An average of 6% is attributed to groundwater seepage through the model attributed 89% to subsurface flow constant throughout the catchment. This is not the same as that derived by the isotopes as the isotopes manage to derive varying contributions between catchments. The use of isotope and this numerical modelling still require more work to be used concurrently, as even comparisons with evapotranspiration (ET) in the study of isotopes are necessary in hydrological studies. As such remote sensing can be used for ET determination, as it is not clear whether the ET for the south is higher than the north in this mesoscale catchment.

Isotopic data can be used to refine the conceptual scheme of hydrological models as they can outline some pertinent behaviour in the catchment especially in mesoscale and complicated semi arid catchments as Roxo These processes and water transport processes that were able to be identified from the catchment wide isotope study are crucial for water quality studies as water quality problems not only arise form the surface runoff water but also from ground water.

It was noted that groundwater flow to the streams and the reservoir is still evident at a substantial ratio. It was finally concluded that the baseflow could be emanating from the escarpment in the northern part of the Roxo catchment and that the effects of evaporation are evidently noticed in the Roxo reservoir which is well mixed. This approach is able to show that in the dry season, deep groundwater from geologic formations is a major importance to baseflow in the catchment

Due to the uncertainty derived form both methods it is recommended that an uncertainty analysis on water source partitioning can be performed on the isotopic mixing model. This can be achieved by a detailed isotopic water balance incorporating spatial and temporal variations in evapotranspiration. The general tendency is to generalise when modelling but in cases when accurate process description is needed in modelling, isotopes can show the differences that would have been ignored. Specific literature where the use of RAM model is incorporated in studies on water source allocation was not available. As such not enough data is available form literature that can be useful for evaluation of the model for such catchments as the Roxo catchment.

Many more factors are at play in Roxo catchment and a more detailed study is recommended for accurate results especially in sensitive issues as water quality, such should incorporate an isotopic water balance study and more sampling points in the reservoir and sampling wells in the southern catchment. Also sampling at more times during the year and some more precipitation samples should be collected for stable water isotopes.

The most essential successes highlighted for this research is that isotopes can be used to understand mesoscale catchment hydrology processes because of their power to quantitatively indicate mesoscale scale variability. This yields an effective indication of catchment scale processes through stable water isotopes interpretation. However explanations of stream hydrochemical behaviour, that were not covered very thoroughly by this research, will continue requiring careful integration of results from the hydrologic, isotopic and geochemical methods rather than the use of any approach in isolation and this has to be taken into account of in any research.

On a concluding note it is recommended to take further these two concepts and use the isotopes to parameterise the water quality hydrology of such a mesoscale catchment as Roxo. To eventually be able to conclude on how resources can be channelled in terms of water management in Roxo reservoir catchment.

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Appendices

Appendix 1 Maps

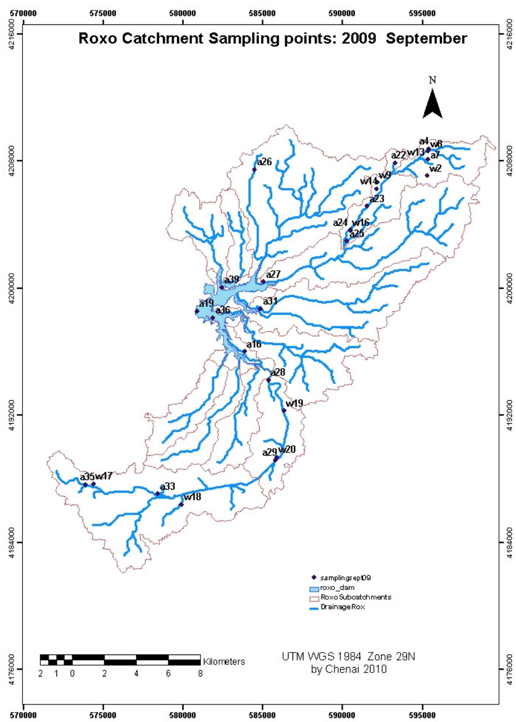


Figure I

Sampling points2009-2009

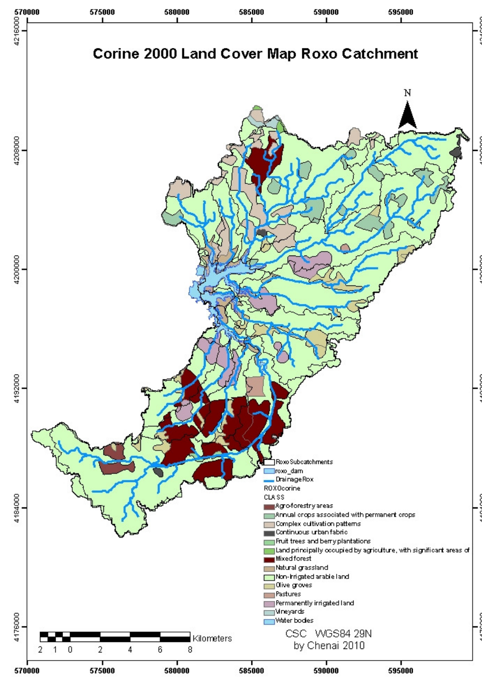


Figure II

Generalised CORINE Land cover map

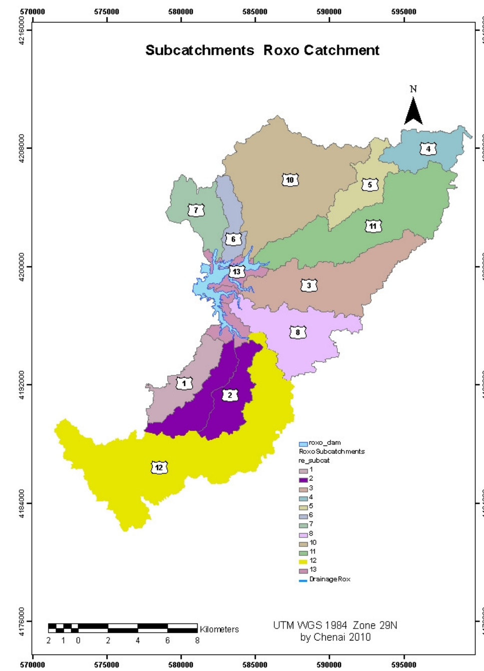


Figure III

Roxo subcatchment used in the RAM model and the source partitioning

Figure III: general maps

Appendix 2: stable water isotope maps

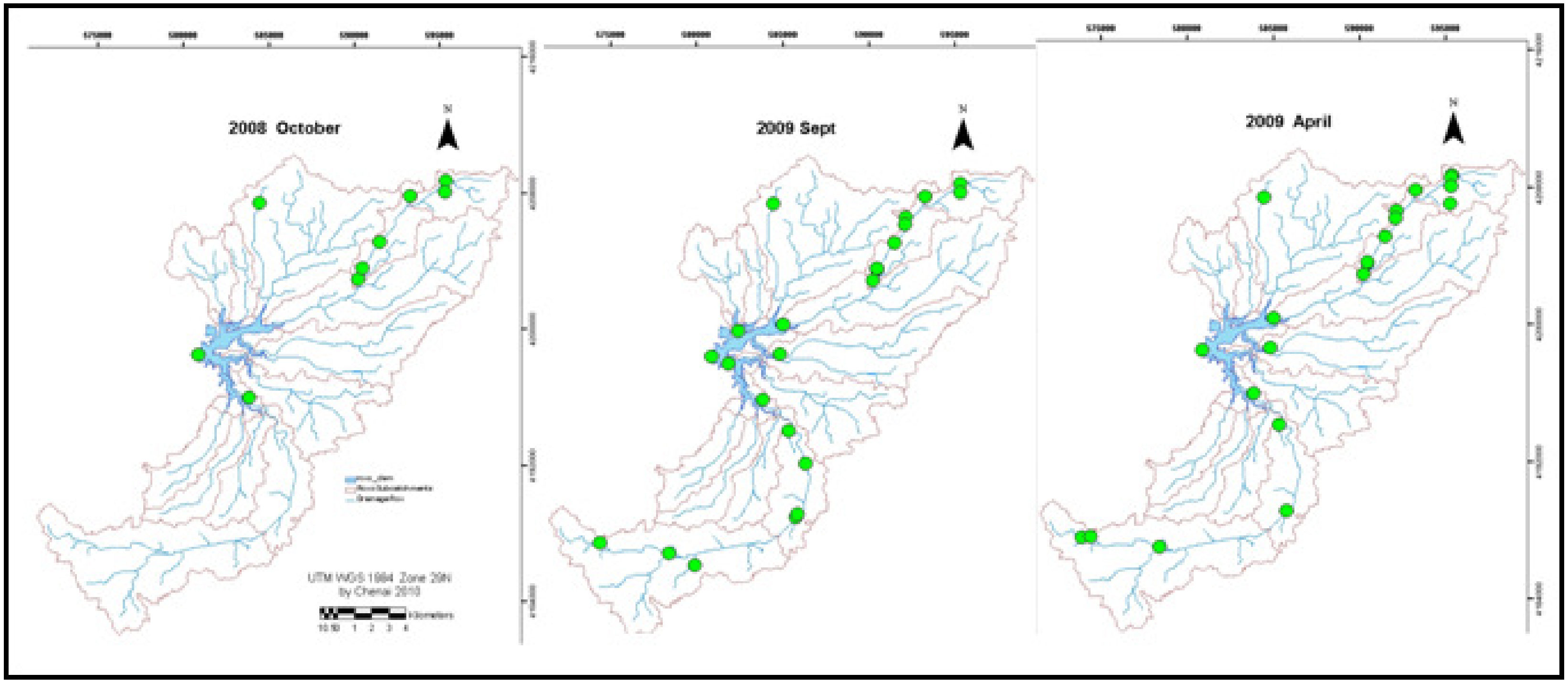
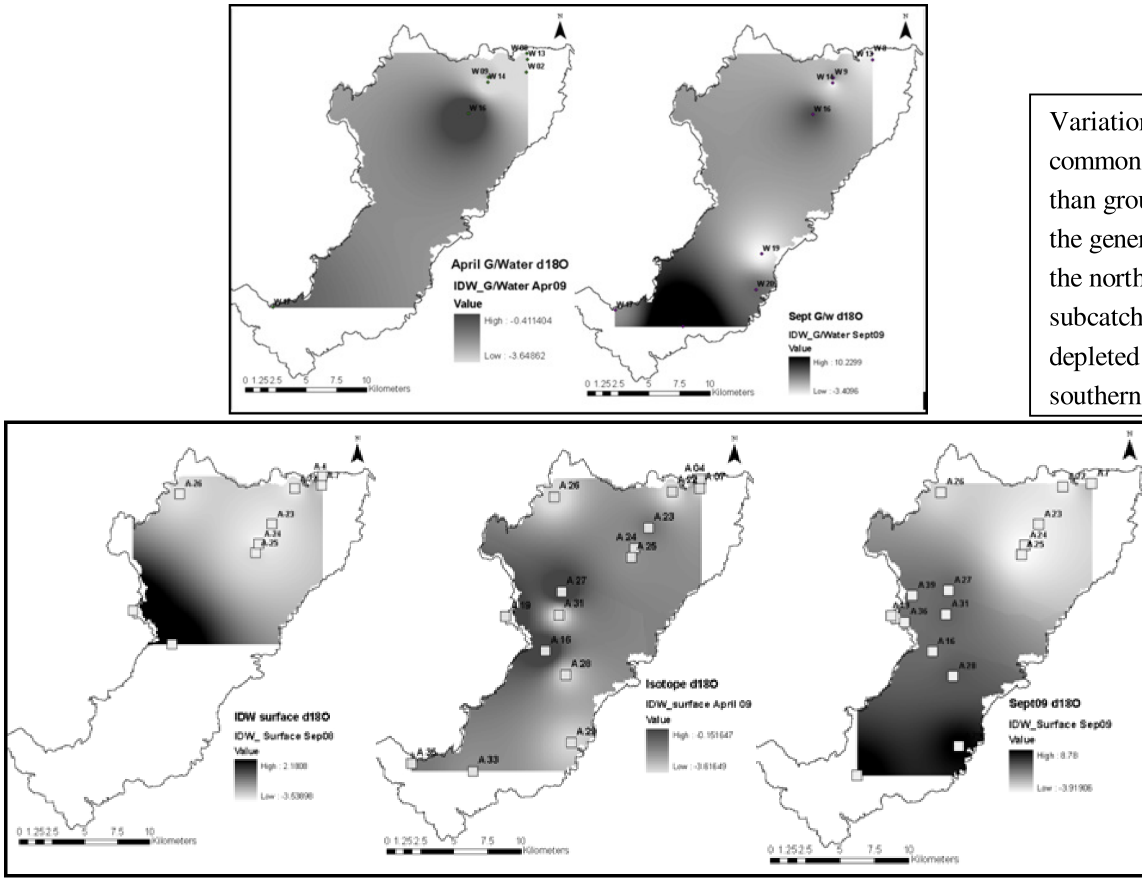


Figure IV: Isotope sampling points distribution over the study season



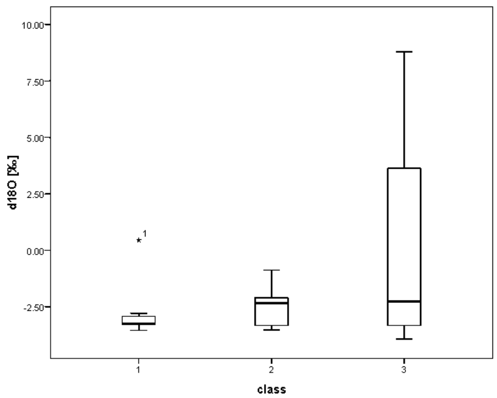
Variations are more common in surface water than groundwater with the general trend being the northern subcatchment more depleted than the southern

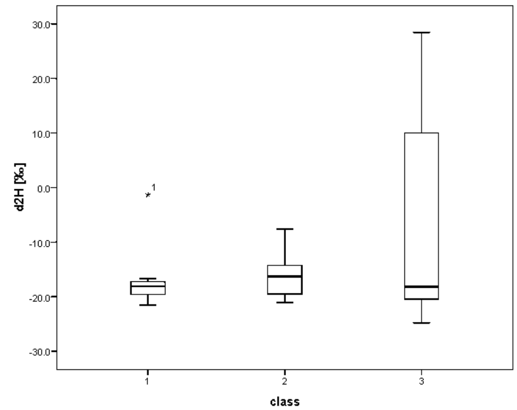
Figure XVI: The temporal and spatial variation of the isotope ($\delta^{18}O$) enrichment in Roxo catchment using Inverse weighted distance (IWD) interpolation method groundwater and surface water. Dark is hign and grey to white is depletion(low isotopic enrichment)

Appendix 3: Isotope Kruskal Wallis Test SPSS and Box and whisker plots

Seasons 1, 2, 3 are the sampling period 2008 October, 2009 April and 2009 September respectively The box and whisker plots indicate the lower quartile and the upper quartile by their outer lines on the box. The middle line represents the median and the whiskers indicate the spread of the data, based on approximately 1.5times the interquartile range.

1) <u>Streams</u>





d18O [‰] **d2H [‰]**

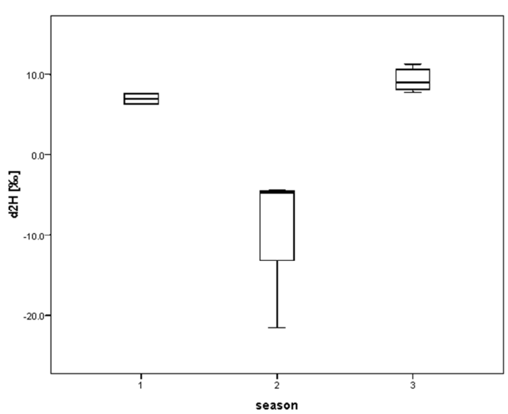
Test Statistics[a,b]

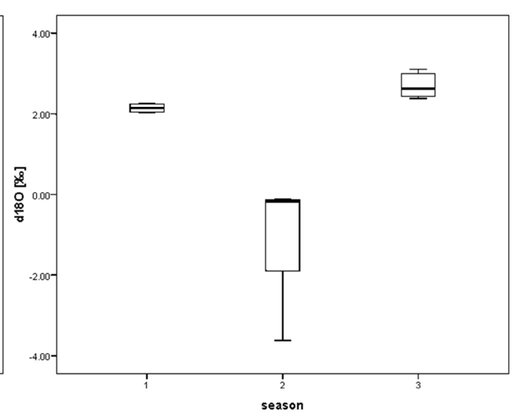
	d18O [‰]	d2H [‰]
Chi-Square	.836	.196
df	2	2
Asymp. Sig.	.658	.907

a. Kruskal Wallis Test

b. Grouping Variable: class

2) <u>Reservoir</u>





d2H [‰] **d18O [‰]**

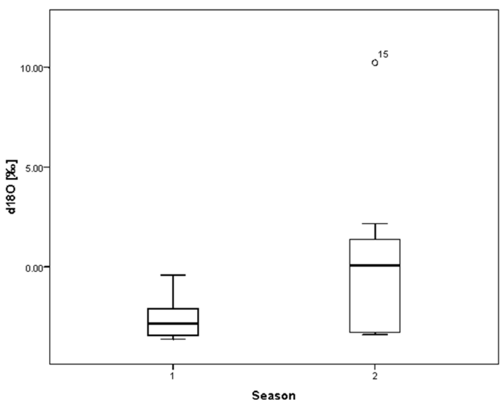
Test Statistics[a,b]

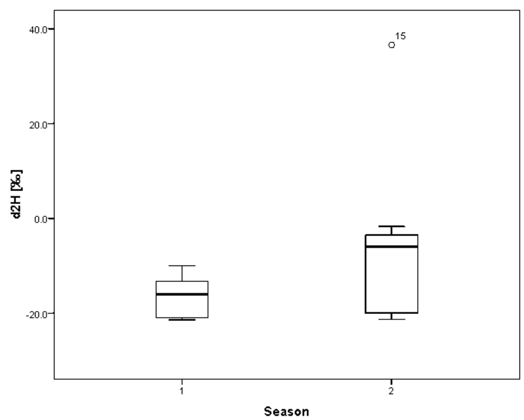
	d2H [‰]	d18O [‰]
Chi-Square	9.231	9.231
df	2	2
Asymp. Sig.	.010	.010

a. Kruskal Wallis Test

b. Grouping Variable: season

3) Wells





d18O [‰] **d2H [‰]**

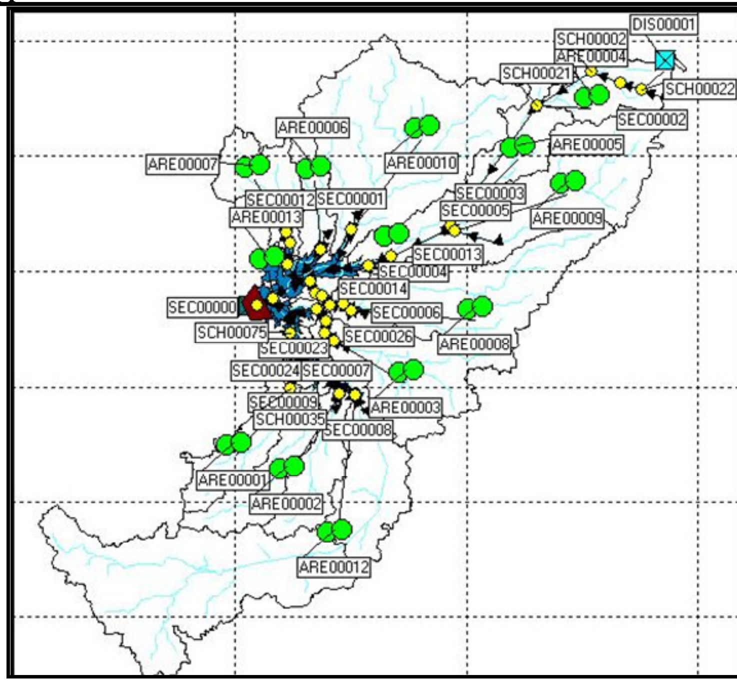
Test Statistics[a,b]

	d2H [‰]	d18O [‰]
Chi-Square	1.751	2.873
df	1	1
Asymp. Sig.	.186	.090

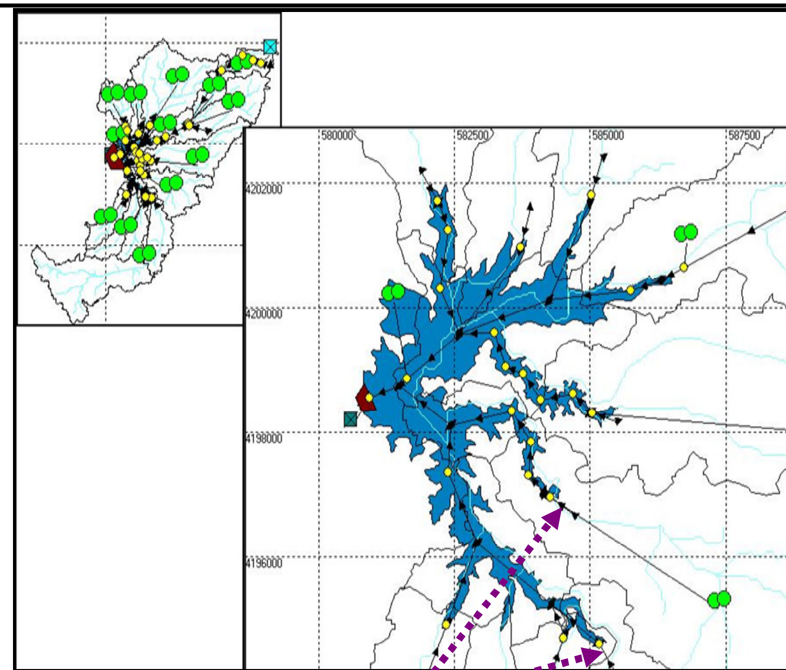
a. Kruskal Wallis Test

b. Grouping Variable: Season

Appendix 4: RAM Areas used in DUFLOW



A
RAM areas (green double circles) used in source allocation analysis to the Roxo Reservoir



B
The inflow points to the Roxo (yellow dots at tips of reservoir inflows) from the various subcatchments represented by the Ram Areas

Figure VI: Figure VII: figure showing the RAM areas (green double circles) used in source allocation analysis to the Roxo Reservoir. Map B shows the inflows to the Roxo (yellow dots at tips of reservoir inflows) from the various subcatchments represented by the Ram Areas.

Appendix 5: Land cover samples

Figure VIII: Land use pictures observed during fieldwork

Appendix 6: Discharge measurements experiment

DETERMINATION OF DISCHARGE (Q)

NOTE:

A 400g of harmless table salt was used

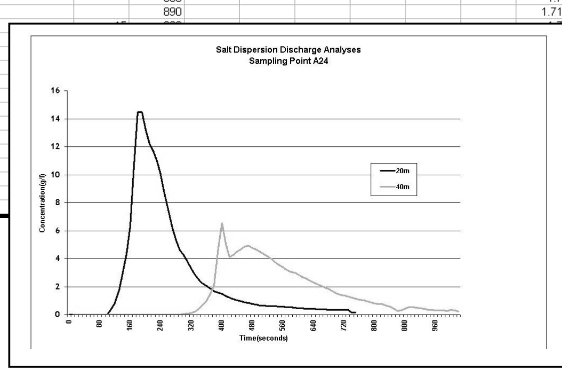
B Covertion factor from EC (mS/cm) to concentration (g/l) **0.67**

C C- Total salt concentration (background and added)

D C2- Salt concentration measured excluding background

E Integral is a result of applying trapezium rule

RAW DATA MEASURED AT SITE (ELECTRICAL CONDUCTIVITY)		20m	40m	SECONDARY DATA AT 20 M		30m		400g			SECONDARY DATA AT 40 M 60m	350g		
Time(min	Time(s)	EC(µS/cm	EC(µS/cm)	Time(min	Time(s)	EC(mS/cn	C (g/l)	C2 (g/l)	Integral	Q (l/s)	EC(mS/cn	C (g/l)	C2 (g/l)	Integral
0	0	1606	1633	0	0	1.606	1.07602	0		**2.05885**	1.633	1.09411	0	
	10	1606	1633		10	1.606	1.07602	0	0		1.633	1.09411	0	0
	20	1606	1633		20	1.606	1.07602	0	0		1.633	1.09411	0	0
	30	1606	1633		30	1.606	1.07602	0	0		1.633	1.09411	0	0
	40	1606	1633		40	1.606	1.07602	0	0		1.633	1.09411	0	0
	50	1606	1633		50	1.606	1.07602	0	0		1.633	1.09411	0	0
1	60	1606	1633	1	60	1.606	1.07602	0	0		1.633	1.09411	0	0
	70	1606	1633		70	1.606	1.07602	0	0		1.633	1.09411	0	0
	80	1606	1633		80	1.606	1.07602	0	0		1.633	1.09411	0	0
	90	1606	1633		90	1.606	1.07602	0	0		1.633	1.09411	0	0
	100	1606	1633		100	1.606	1.07602	0	0		1.633	1.09411	0	0
	110	1606	1633		110	1.606	1.07602	0	0		1.633	1.09411	0	0
2	120	1720	1633	2	120	1.72	1.1524	0.07638	0.3819		1.633	1.09411	0	0
	130	1728	1633		130	1.728	1.15776	0.08174	0.7906		1.633	1.09411	0	0
	140	1999	1633		140	1.999	1.33933	0.26331	1.72525		1.633	1.09411	0	0
	150	2100	1633		150	2.1	1.407	0.33098	2.97145		1.633	1.09411	0	0
	160	2400	1633		160	2.4	1.608	0.53198	4.3148		1.633	1.09411	0	0
	170	2700	1633		170	2.7	1.809	0.73298	6.3248		1.633	1.09411	0	0
3	180	3700	1633	3	180	3.7	2.479	1.40298	10.6798		1.633	1.09411	0	0
	190	3830	1633		190	3.83	2.5661	1.49008	14.4653		1.633	1.09411	0	0
	200	3700	1633		200	3.7	2.479	1.40298	14.4653		1.633	1.09411	0	0
	210	3460	1633		210	3.46	2.3182	1.24218	13.2258		1.633	1.09411	0	0
	220	3400	1633		220	3.4	2.278	1.20198	12.2208		1.633	1.09411	0	0
	230	3300	1633		230	3.3	2.211	1.13498	11.6848		1.633	1.09411	0	0
4	240	3200	1633	4	240	3.2	2.144	1.06798	11.0148		1.633	1.09411	0	0
	250	3000	1633		250	3	2.01	0.93398	10.0098		1.633	1.09411	0	0
	260	2810	1633		260	2.81	1.8827	0.80668	8.7033		1.633	1.09411	0	0
	270	2600	1633		270	2.6	1.742	0.66598	7.3633		1.633	1.09411	0	0
	280	2460	1633		280	2.46	1.6482	0.57218	6.1908		1.633	1.09411	0	0
	290	2330	1633		290	2.33	1.5611	0.48508	5.2863		1.633	1.09411	0	0
5	300	2260	1639	5	300	2.26	1.5142	0.43818	4.6163		1.639	1.09813	0.00402	0.0201
	310	2220	1645		310	2.22	1.4874	0.41138	4.2478		1.645	1.10215	0.00804	0.0603
	320	2130	1656		320	2.13	1.4271	0.35108	3.8123		1.656	1.10952	0.01541	0.11725
	330	2050	1675		330	2.05	1.3735	0.29748	3.2428		1.675	1.12225	0.02814	0.21775
	340	2000	1721		340	2	1.34	0.26398	2.8073		1.721	1.15307	0.05896	0.4355
	350	1955	1755		350	1.955	1.30985	0.23383	2.48905		1.755	1.17585	0.08174	0.7035
6	360	1922	1805	6	360	1.922	1.28774	0.21172	2.22775		1.805	1.20935	0.11524	0.9849
	370	1903	1900		370	1.903	1.27501	0.19899	2.05355		1.9	1.273	0.17889	1.47065
	380	1870	1997		380	1.87	1.2529	0.17688	1.87935		1.997	1.33799	0.24388	2.11385
	390	1842	2690		390	1.842	1.23414	0.15812	1.675		2.69	1.8023	0.70819	4.76035
	400	1834	2537		400	1.834	1.22878	0.15276	1.5544		2.537	1.69979	0.60568	6.56935
	410	1816	2240		410	1.816	1.21672	0.1407	1.4673		2.24	1.5008	0.40669	5.06185
7	420	1794	2250	7	420	1.794	1.20198	0.12596	1.3333		2.25	1.5075	0.41339	4.1004
	430	1779	2290		430	1.779	1.19193	0.11591	1.20935		2.29	1.5343	0.44019	4.2679
	440	1765	2320		440	1.765	1.18255	0.10653	1.1122		2.32	1.5544	0.46029	4.5024
	450	1751	2350		450	1.751	1.17317	0.09715	1.0184		2.35	1.5745	0.48039	4.7034
	460	1742	2370		460	1.742	1.16714	0.09112	0.94135		2.37	1.5879	0.49379	4.8709
	470	1735	2360		470	1.735	1.16245	0.08643	0.88775		2.36	1.5812	0.48709	4.9044
8	480	1725	2330	8	480	1.725	1.15575	0.07973	0.8308		2.33	1.5611	0.46699	4.7704
	490	1720	2320		490	1.72	1.1524	0.07638	0.78055		2.32	1.5544	0.46029	4.6364
	500	1709	2290		500	1.709	1.14503	0.06901	0.72695		2.29	1.5343	0.44019	4.5024
	510	1702	2260		510	1.702	1.14034	0.06432	0.66665		2.26	1.5142	0.42009	4.3014
	520	1698	2240		520	1.698	1.13766	0.06164	0.6298		2.24	1.5008	0.40669	4.1339
	530	1693	2210		530	1.693	1.13431	0.05829	0.59965		2.21	1.4807	0.38659	3.9664
9	540	1703	2170	9	540	1.703	1.14101	0.06499	0.6164		2.17	1.4539	0.35979	3.7319
	550	1696	2150		550	1.696	1.13632	0.0603	0.62645		2.15	1.4405	0.34639	3.5309
	560	1692	2130		560	1.692	1.13364	0.05762	0.5896		2.13	1.4271	0.33299	3.3969
	570	1689	2090		570	1.689	1.13163	0.05561	0.56615		2.09	1.4003	0.30619	3.1959
	580	1685	2090		580	1.685	1.12895	0.05293	0.5427		2.09	1.4003	0.30619	3.0619
	590	1681	2080		590	1.681	1.12627	0.05025	0.5159		2.08	1.3936	0.29949	3.0284
10	600	1678	2040	10	600	1.678	1.12426	0.04824	0.49245		2.04	1.3668	0.27269	2.8609
	610	1675	2030		610	1.675	1.12225	0.04623	0.47235		2.03	1.3601	0.26599	2.6934
	620	1670	2010		620	1.67	1.1189	0.04288	0.44555		2.01	1.3467	0.25259	2.5929
	630	1669	1980		630	1.669	1.11823	0.04221	0.42545		1.98	1.3266	0.23249	2.4254
	640	1668	1973		640	1.668	1.11756	0.04154	0.41875		1.973	1.32191	0.2278	2.30145
	650	1666	1939		650	1.666	1.11622	0.0402	0.4087		1.939	1.29913	0.20502	2.1641
11	660	1663	1938	11	660	1.663	1.11421	0.03819	0.39195		1.938	1.29846	0.20435	2.04685
	670	1662	1910		670	1.662	1.11354	0.03752	0.37855		1.91	1.2797	0.18559	1.9497
	680	1659	1897		680	1.659	1.11153	0.03551	0.36515		1.897	1.27099	0.17688	1.81235
	690	1659	1875		690	1.659	1.11153	0.03551	0.3551		1.875	1.25625	0.16214	1.6951
	700	1659	1851		700	1.659	1.11153	0.03551	0.3551		1.851	1.24017	0.14606	1.541
	710	1659	1841		710	1.659	1.11153	0.03551	0.3551		1.841	1.23347	0.13936	1.4271
12	720	1659	1836	12	720	1.659	1.11153	0.03551	0.3551		1.836	1.23012	0.13601	1.37685
	730	1656	1820		730	1.656	1.10952	0.0335	0.34505		1.82	1.2194	0.12529	1.3065
	740	1655	1809		740	1.655	1.10885	0.03283	0.33165		1.809	1.21203	0.11792	1.21605
	750	1600	1799		750	1.6	1.072	-0.00402	0.14405		1.799	1.20533	0.11122	1.1457
	760	1659	1790		760	1.659	1.11153	0.03551	0.15745		1.79	1.1993	0.10519	1.08205
	770		1785		770				**194.2833**		1.785	1.19595	0.10184	1.03515
13	780		1765	13	780						1.765	1.18255	0.08844	0.9514
	790		1759		790						1.759	1.17853	0.08442	0.8643
	800		1750		800						1.75	1.1725	0.07839	0.81405
	810		1744		810						1.744	1.16848	0.07437	0.7638
	820		1750		820						1.75	1.1725	0.07839	0.7638
	830		1715		830						1.715	1.14905	0.05494	0.66665
14	840		1726	14	840						1.726	1.15642	0.06231	0.58625
	850		1664		850						1.664	1.11488	0.02077	0.4154
	860		1682		860						1.682	1.12694	0.03283	0.268
	870		1680		870						1.68	1.1256	0.03149	0.3216
	880		1710		880						1.71	1.1457	0.05159	0.4154
	890		1715		890						1.715	1.14905	0.05494	0.53265
15	900		1710									1.1457	0.05159	0.53265
	910		1705									1.14235	0.04824	0.49915
	920		1700									1.139	0.04489	0.46565
	930		1687									1.13029	0.03618	0.40535
	940		1682									1.12694	0.03283	0.34505
	950		1681									1.12627	0.03216	0.32495
16	960		1680									1.1256	0.03149	0.31825
	970		1680									1.1256	0.03149	0.3149
	980		1675									1.12225	0.02814	0.29815
	990		1674									1.12158	0.02747	0.27805
	1000		1689									1.13163	0.03752	0.32495
	1010		1668									1.11756	0.02345	0.30485
17	1020		1668									1.11756	0.02345	0.2345
														140.8039



Appendix 7: Isotopes data

Table X: Stable water isotopes Analysis results

Sample nr.	Date	Descripti	δ^2H [‰]	δ^{18}O [‰]	d [‰]
154431	Sep-08	**A-4**	-1.3	0.45	-4.9
154432	Sep-08	**A-7**	-17.8	-3.26	8.3
154433	Sep-08	**A-16**	6.3	2.04	-10.0
154434	Sep-08	**A-19**	7.6	2.26	-10.5
154435	Sep-08	**A-22**	-18.1	-3.34	8.6
154436	Sep-08	**A-23**	-19.7	-3.25	6.3
154439	Sep-08	**A-24**	-21.5	-3.54	6.8
154437	Sep-08	**A-25**	-16.7	-2.79	5.6
154438	Sep-08	**A-26**	-19.5	-3.05	4.9
		minimum	-21.50	-3.54	-10.48
		maximum	7.60	2.26	8.62
		mean	-11.19	-1.61	1.68

Sample nr.	Date	Descripti	δ^2H [‰] ± 1,0	δ^{18}O [‰] ± 0,1	d [‰]
156328	Apr-09	**A 04**	-7.6	-0.88	-0.6
156329	Apr-09	**A 07**	-19.5	-3.44	8.0
156330	Apr-09	**A 16**	-4.8	-0.18	-3.4
156331	Apr-09	**A 19**	-4.6	-0.11	-3.7
156332	Apr-09	**A 22**	-19.5	-3.52	8.7
156333	Apr-09	**A 23**	-12.6	-1.86	2.3
156334	Apr-09	**A 24**	-14.2	-2.25	3.8
156335	Apr-09	**A 25**	-15.9	-2.33	2.7
156336	Apr-09	**A 26**	-21.1	-3.45	6.5
156327	Apr-09	**A 27**	-4.4	-0.15	-3.2
156337	Apr-09	**A 28**	-19.6	-3.21	6.1
156338	Apr-09	**A 29**	-20.2	-3.19	5.3
156339	Apr-09	**A 31**	-21.5	-3.62	7.5
156340	Apr-09	**A 33**	-16.3	-2.32	2.3
156341	Apr-09	**A 35**	-14.3	-1.94	1.2
156342	Apr-09	**W 02**	-16.1	-2.87	6.9
156344	Apr-09	**W 08**	-21.4	-3.65	7.8
156343	Apr-09	**W 09**	-14.2	-2.48	5.6
156345	Apr-09	**W 13**	-20.8	-3.51	7.3
156346	Apr-09	**W 14**	-21.1	-3.42	6.3
156347	Apr-09	**W 16**	-10.0	-0.41	-6.7
156348	Apr-09	**W 17**	-12.3	-1.74	1.6
		minimum	-21.50	-3.65	-6.72
		maximum	-4.40	-0.11	8.66
		mean	-15.09	-2.30	3.28

Sample nr.	Date	Descripti	δ2H [‰] ± 1,0	δ18O [‰] ± 0,1	δ [‰]
159211	07.09.2009	**A 07**	-10.8	-0.94	-3.3
159212	08.09.2009	**A 16**	9.3	2.66	-12.0
159213	09.09.2009	**A 19**	8.1	2.39	-11.0
159214	11.09.2009	**A 22**	-19.6	-3.34	7.1
159215	08.09.2009	**A 23**	-20.5	-3.25	5.6
159216	08.09.2009	**A 24**	-24.8	-3.92	6.6
159217	09.09.2009	**A 25**	-22.8	-3.80	7.7
159218	10.09.2009	**A 26**	-18.2	-2.25	-0.2
159219	08.09.2009	**A 27**	10.6	3.01	-13.5
159220	12.09.2009	**A 28**	10.0	3.64	-19.1
159221	11.09.2009	**A 29**	22.7	7.80	-39.8
159222	11.09.2009	**A 31**	11.3	3.11	-13.6
159223	10.09.2009	**A 33**	28.5	8.78	-41.8
159224	09.09.2009	**A 36**	7.8	2.44	-11.8
159225	12.09.2009	**A 39**	8.8	2.60	-12.1
159226	07.09.2009	**W 08**	-20.9	-3.41	6.4
159227	08.09.2009	**W 09**	-3.5	0.30	-5.9
159228	07.09.2009	**W 13**	-18.2	-2.70	3.4
159229	07.09.2009	**W 14**	-21.3	-3.42	6.1
159230	09.09.2009	**W 16**	-1.7	2.16	-19.0
159231	10.09.2009	**W 17**	-6.0	0.07	-6.6
159232	10.09.2009	**W 18**	36.6	10.23	-45.2
159233	11.09.2009	**W 19**	-20.0	-3.32	6.6
159234	12.09.2009	**W 20**	-5.2	1.37	-16.2
		minimum	-24.80	-3.92	-45.24
		maximum	36.60	10.23	7.65
		mean	-2.50	0.84	-9.24

Table V: Isotope Analysis statistics

2009 Sept		Average	minimum	maximum	standard dev	n
	d^2H [‰]	-6.2	-24.8	28.5	20.8	9
Streams	$d^{18}O$ [‰	0.30	-3.92	8.78	5.10	
	d [‰]	-8.58	-41.79	7.65	20.07	
	d^2H [‰]	-6.7	-21.3	36.6	18.2	9
wells	$d^{18}O$ [‰	0.14	-3.42	10.23	4.37	
	d [‰]	-7.83	-45.24	6.56	17.05	
	d^2H [‰]	9.3	7.8	11.3	1.4	6
roxo reservoir	$d^{18}O$ [‰	2.70	2.39	3.11	0.30	
	d [‰]	-12.33	-13.63	-11.02	1.02	
2009 April	d^2H [‰]	-16.4	-21.1	-7.6	4.1	11
Streams	$d^{18}O$ [‰	-2.58	-3.52	-0.88	0.85	
	d [‰]	4.21	-0.56	8.66	2.93	
	d^2H [‰]	-16.6	-21.4	-10.0	4.6	
wells	$d^{18}O$ [‰	-2.58	-3.65	-0.41	1.17	6
	d [‰]	4.11	-6.72	7.80	5.19	
	d^2H [‰]	-8.8	-21.5	-4.4	8.5	
roxo reservoir	$d^{18}O$ [‰	-1.02	-3.62	-0.11	1.74	4
	d [‰]	-0.71	-3.72	7.46	5.45	
2008 Sept	d^2H [‰]	-16.4	-21.5	-1.3	6.8	7
Streams	$d^{18}O$ [‰	-2.68	-3.54	0.45	1.40	
	d [‰]	5.09	-4.90	8.62	4.60	
	d^2H [‰]	7.0	6.3	7.6	0.9	2
roxo reservoir	$d^{18}O$ [‰	2.15	2.04	2.26	0.16	
	d [‰]	-10.25	-10.48	-10.02	0.33	

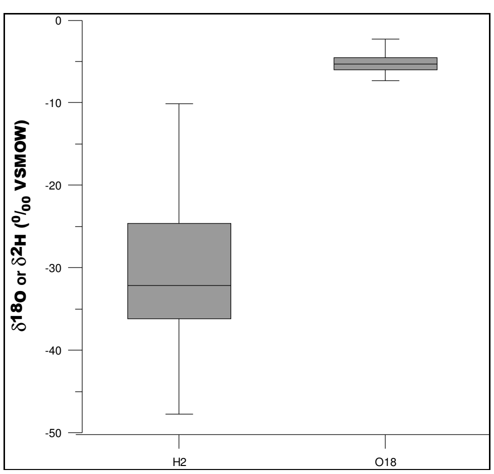


Figure IX: Isotopes in precipitation data distribution, Box and whisker plot @ IAEA /WMO database

Fit results for isotope analyses

LEL April 2009

Fit Results

LEL
Equation Y = 4.864979835 * X - 3.887045467
Number of data points used = 4
Average X = -1.015
Average Y = -8.825
Residual sum of squares = 0.0800054
Regression sum of squares = 214.207
Coef of determination, R-squared = 0.999627
Residual mean square, sigma-hat-sq'd = 0.0400027

Fit Results

wells
Equation Y = 3.75146784 * X - 6.867637352
Number of data points used = 7
Average X = -2.58286
Average Y = -16.5571
Residual sum of squares = 13.2374
Regression sum of squares = 115.74
Coef of determination, R-squared = 0.897366
Residual mean square, sigma-hat-sq'd = 2.64748

Fit Results

streams
Equation Y = 4.707078608 * X - 4.287821666
Number of data points used = 11
Average X = -2.58091
Average Y = -16.4364
Residual sum of squares = 7.70306
Regression sum of squares = 159.662
Coef of determination, R-squared = 0.953975
Residual mean square, sigma-hat-sq'd = 0.855896

LEL Sept 2009

Fit Results

LEL-Sept2009
Equation Y = 4.629678789 * X - 3.22461553
Number of data points used = 6
Average X = 2.70167
Average Y = 9.28333
Residual sum of squares = 0.21848
Regression sum of squares = 9.41985
Coef of determination, R-squared = 0.977332
Residual mean square, sigma-hat-sq'd = 0.0546201

Fit Results

wells
Equation Y = 4.126931394 * X - 7.275830243
Number of data points used = 9
Average X = 0.142222
Average Y = -6.68889
Residual sum of squares = 35.3202
Regression sum of squares = 2601.49
Coef of determination, R-squared = 0.986605
Residual mean square, sigma-hat-sq'd = 5.04574

Fit Results

streams
Equation Y = 4.072284367 * X - 7.397401498
Number of data points used = 9
Average X = 0.302222
Average Y = -6.16667
Residual sum of squares = 16.5283
Regression sum of squares = 3446.49
Coef of determination, R-squared = 0.995227
Residual mean square, sigma-hat-sq'd = 2.36119

LEL Sept 2008

Fit Results

LEL-Sept2008
Equation Y = 5.909090909 * X - 5.754545455
Number of data points used = 2
Average X = 2.15
Average Y = 6.95
Residual sum of squares = 0
Regression sum of squares = 0.846
Coef of determination, R-squared = 1
Residual mean square, sigma-hat-sq'd = 0

Fit Results

streams
Equation Y = 4.80758132 * X - 3.473374687
Number of data points used = 7
Average X = -2.68286
Average Y = -16.3714
Residual sum of squares = 7.1309
Regression sum of squares = 272.323
Coef of determination, R-squared = 0.974483
Residual mean square, sigma-hat-sq'd = 1.42618

Appendix 8: Laboratory Analysis Results

Sample point	X	Y	Temperature °C	pH	HCO3(2-) mmol/litre	HCO3(2-) mg/litre	EC µS/cm	D.O mg/l	CL(-) mg/l	SO4(2-) mg/l	NO3_N mg/l	NO3mg/l	NO2_N mg/l	po4(3-) mg/l	NH3_N mg/l	Si mg/l	Al mg/l	Fe mg/l	Mn mg/l	K mg/l	Ca mg/l	Mg mg/l	Na m
A07	595334	4208084	26.5	10.49	6.2	378.324	543	8.74	36	82.5	11.5	51.1	0.265	0.075	0	6.60	0.07	0.06	<Det.Lim	3.39	26.85	35.07	61.8
A16	583835	4195981	30.2	9.54	4.3	262.386	1454	6.69	352	65	1.5	6.7		0.075	0.35	0.475	0.155	0.17	0.03	6.82775	73.61	49.19	123.8
A19	580863	4198543	27.8	9.61	3	183.06	1392	7.26	340	72.5	2	8.8		0.045	0.4	0.25	0.06	<Det.Lim	<Det.Lim	7.35205	84.69	64.84	158.2
A19(rep)	580863	4198543	27.8	9.61	3	183.06	1392	7.26	340	67.5	1.7	7.6	0.003	0.02	0.15	0.24	0.07	<Det.Lim	<Det.Lim	8.0087	83.54	49.26	119.3
A23	591530	4205136	21.4	9.25	7.3	445.446	1114	6.5	130	66.25	5.4	23.9		0.735	0.15	7.795	0.075	<Det.Lim	<Det.Lim	7.05639	71.81	49.77	123.0
A24	590483	4203625	21.9	9.19	8.9	543.078	1614	8.6	274	75	4.2	18.4		0.125	0.25	7.52	0.08	<Det.Lim	0.01	3.11205	122.7	66.07	115.7
A26	584458	4207448	19.1	9.18	8.2	500.364	1032	5.27	90	63.5	3.9	17.1		3.82	0.45	9.69	0.08	0.02	0.04	12.6028	87.04	66.45	88.1
A27	585011	4200365	28.3	9.81	4.3	262.386	1452	8.47	380	81.25	1.2	5.1		0.015	0.15	0.51	0.08	0.01	<Det.Lim	7.95001	57.7	52.97	130.1
A29	585748	4189147	27.8	9.4	3.9	237.978	3300	7.1	978	115	1.7	7.7	0.002	0.035	0.05	0.315	0.135	0.135	0.11	13.9346	93.17	130.71	348.6
A31	584832	4198656	30.4	9.86	2.8	170.856	1469	9.58	360	71	2	8.6		0.115	0.2	0.575	0.245	0.475	0.14	7.14927	67.73	51.17	129.8
A33	578416	4187026	26.5	10.71	4.3	262.386	1603	12.04	390	85	6.4	29.4	0.002	0.09	0	0.865	0.05	0.04	0.04	5.48495	28.04	57.95	201.8
W08	595336	4208581	20.9	8.81	5.3	323.406	751	5.52	34	75	12.5	55.5		0.11	0.45	9.10	0.06	<Det.Lim	<Det.Lim	1.57	79.59	42.98	55.3
W09	592151	4206624	24.4	10.13	4.3	262.386	633	8.8	40	70	6.6	29.1	0.127	0.1	0.2	10.38	0.03	<Det.Lim	<Det.Lim	8.86246	23.24	61.84	66.0
W13	595291	4207047	20.8	8.87	4.8	292.896	798	5.26	26	80	15.7	69.4		0.115	0	6.24	0.07	<Det.Lim	<Det.Lim	2.22983	92.97	40.73	45.3
W14	592116	4206212	21.6	8.78	6.3	384.426	811	6.35	52	60	26.9	119	0.014	0.105	0.05	10.32	0.065	<Det.Lim	<Det.Lim	2.51788	88.45	55.69	54.0
BLANK										0	0.1			0.03		3.17	0.00	0.00	<Det.Lim				

Appendix 9: Geology of study area: Gabbros of Beja Aquifer system

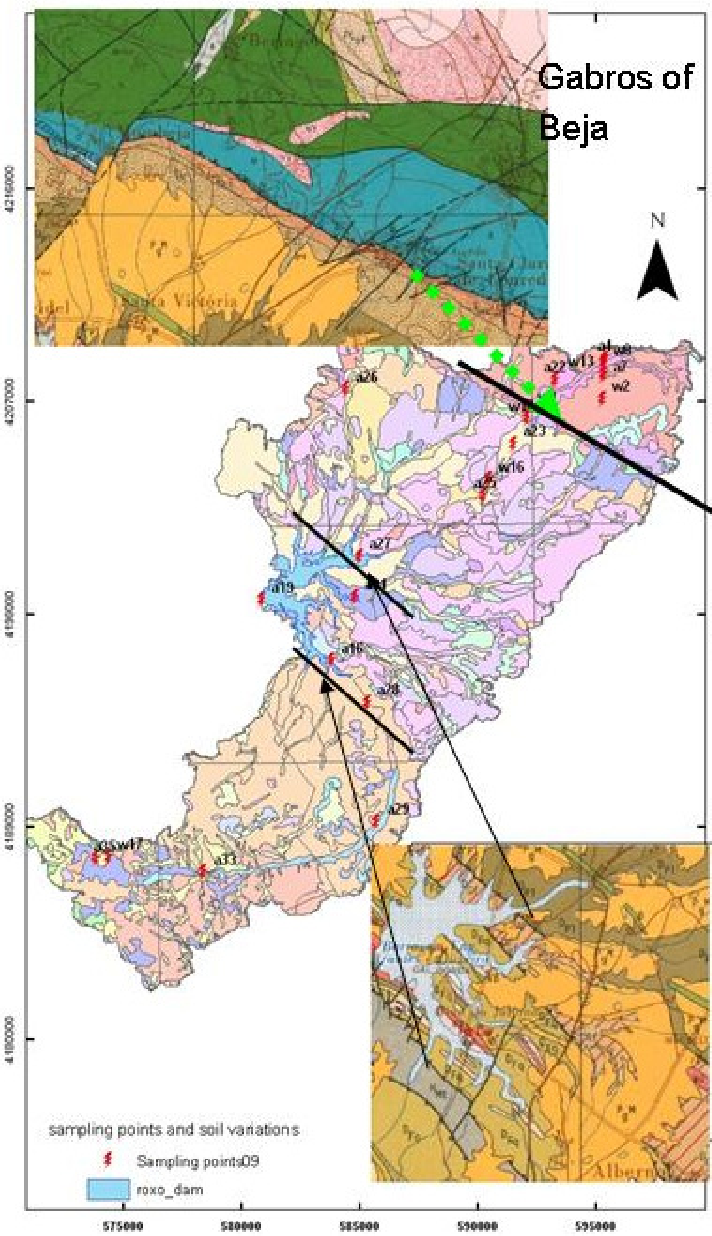


Figure XIV: Positions of the faults escarpment in the Beja district of the Alentejo province

The major fault or escarpment indicated on the map separates the Beja mafic-ultramafic complex constituting the amphibolites and the gabbros. Then a gradual transition going further down south into the phylites and quartzite from the Pulo do lobo. Most of the area in the catchment is overlain by younger palagene layers. The layers of sediments, sandstone and marls and sometimes clays (atapulgite) exist. The non reactive gabbros of Beja make a good aquifer system reported in literature (Paralta, 2005), which has effects on the northern parts of the catchment. Faults also present in the south of the catchment shown from the geologic map *Carta geologica do*

Carta geologica do Sul de Portugal: Scale of 1:200 000, Servicos Geologicos de Portugal Lisbon, 1989, ministry of industry and energy, Director General of Geology and mines