



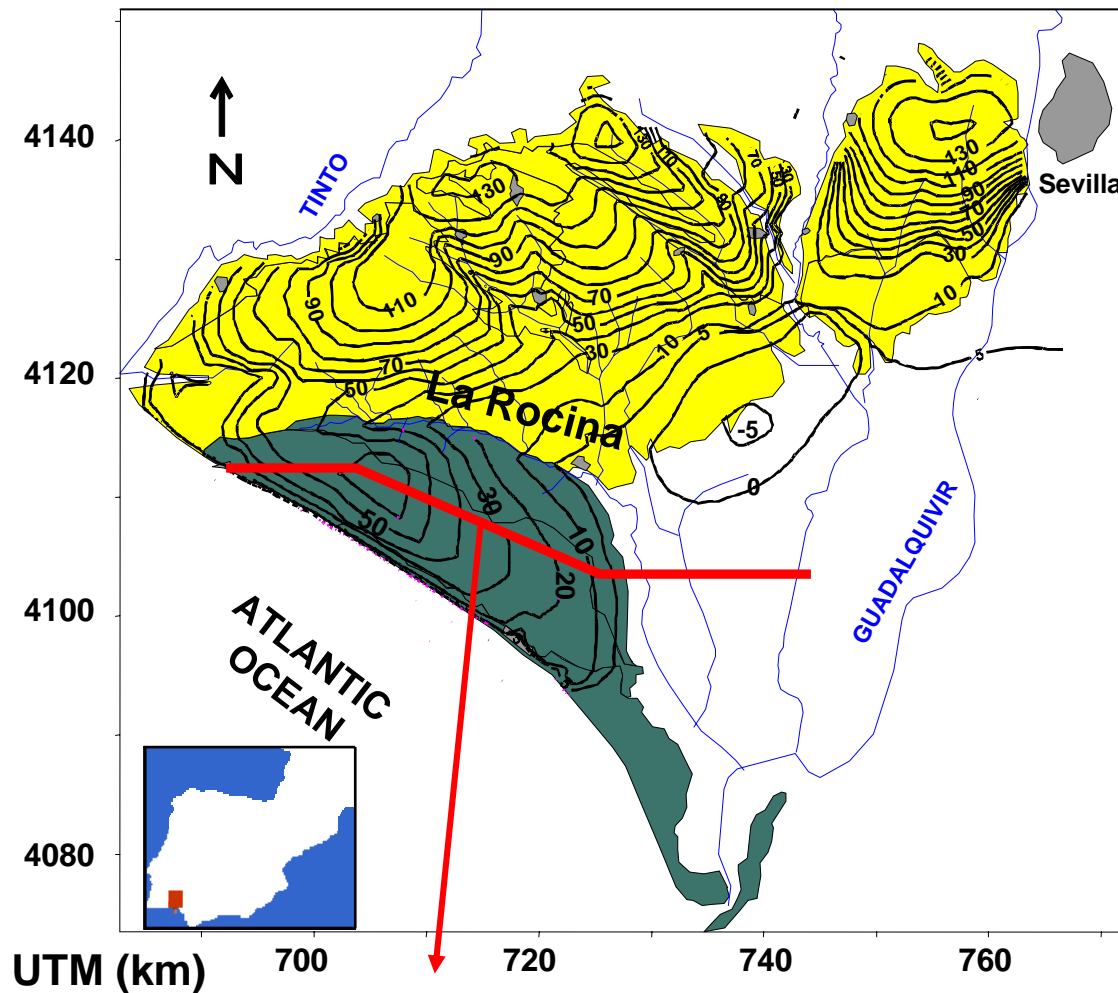
Isotopic assessment of the impact of agriculture on the hydrology of the aquifer and wetlands at the Doñana Ramsar site, SW Spain

H. Higuera¹; M. Manzano¹; E. Custodio²; I. Juárez³; R. Puig⁴; R. Aravena⁵
¹ UPCT, Cartagena, Spain; ² UPC, Barcelona, Spain; ³ AMPHOS 21, Chile;
⁴ UB, Barcelona, Spain; ⁵ UW, Waterloo, Canada

OUTLINE

- 1. Background to aquifer hydrogeology**
- 2. Materials and methods**
- 3. Groundwater flow modifications due to abstractions for irrigation**
- 4. Hydrochemical impact of agriculture. Input and fate of S and N**
- 5. Main conclusions**

1. Background to aquifer hydrogeology



PLIO-QUATERNARY

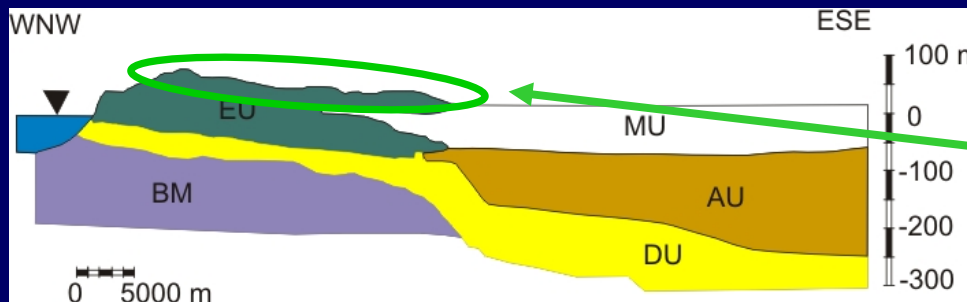
- MU. Marsh Unit: clay
- EU. Eolian Unit: sand
- DU. Deltaic Unit: sand and silt
- AU. Alluvial Unit: sand and gravel

TERTIARY (Miocene)

- BM. Blue marls
- River/Watercourse

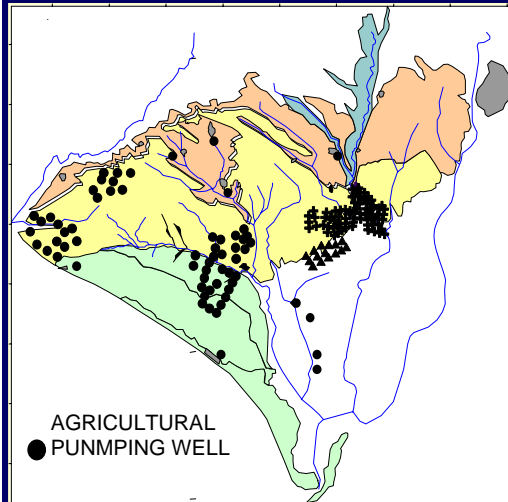
Main natural discharge areas:

- Contact sands-clays (= marshes)
- La Rocina and other watercourses
- Coastline
- Evapotranspiration



Upper part of green (EU) unit:
Large eolian mantle holding
hundreds of small wetlands

1. Background to aquifer hydrogeology



Use of groundwater

1940–1945 Extensive eucalyptus plantation ~100 km²
Now partially eradicated

1970–1985 Irrigation with local GW ~80 km²
Now steady → 100 hm³/a

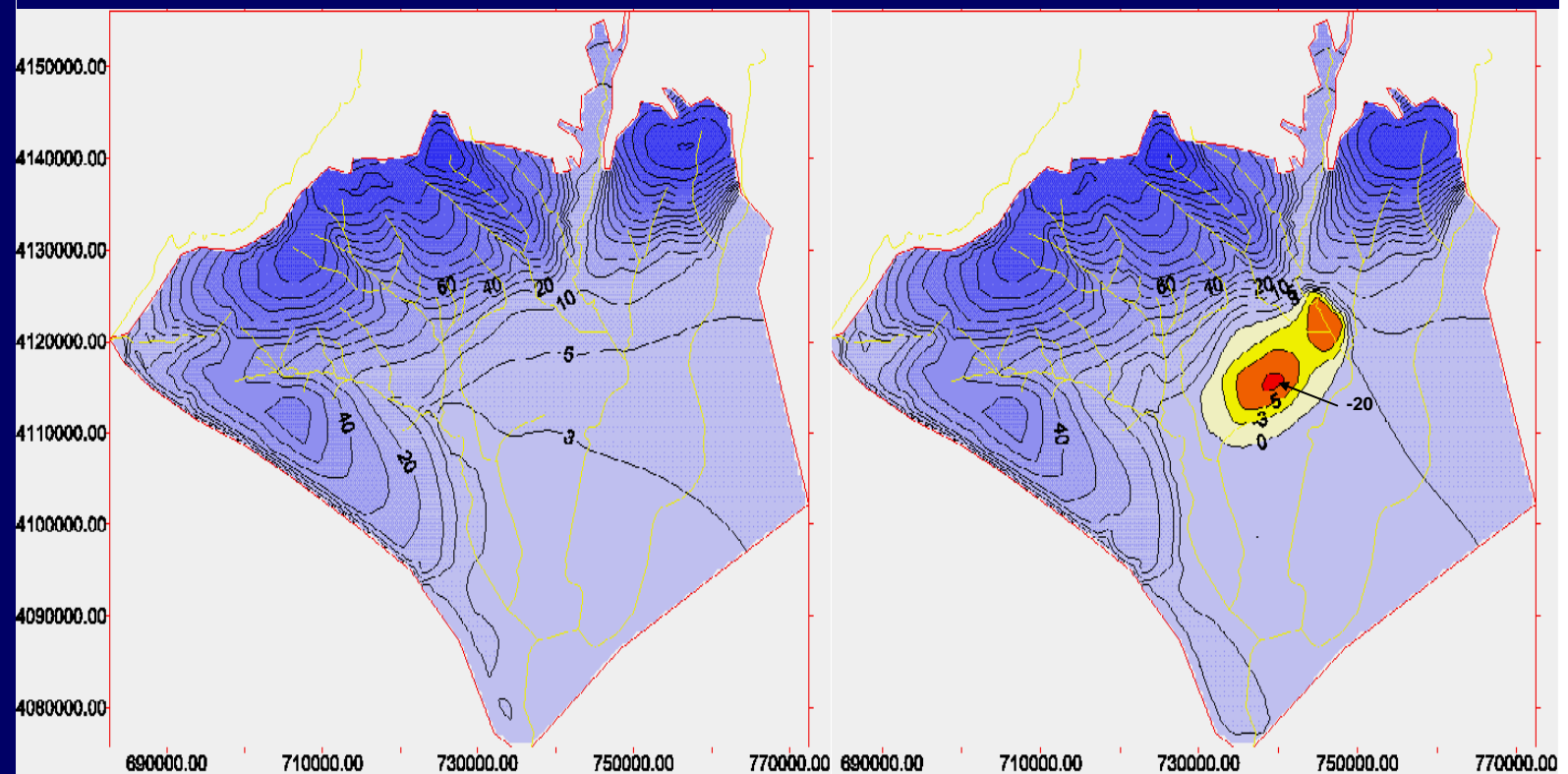
REGIONAL PIEZOMETRY

October 1972

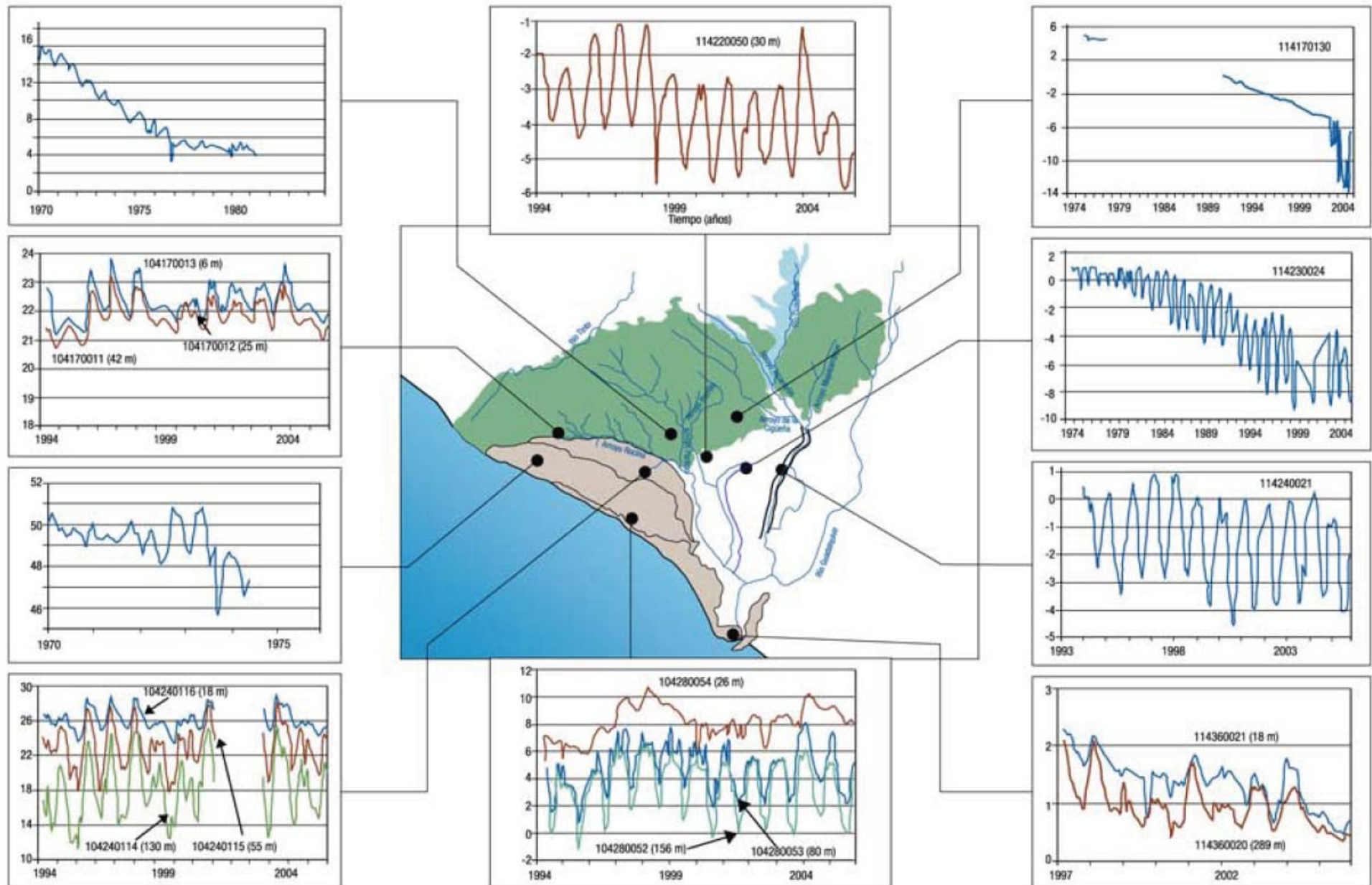
NATURAL CONDITIONS

October 1999

DISTURBED CONDITIONS



1. Background to aquifer hydrogeology



2. Materials and methods

MATERIALS

- Phreatic and piezometric recording at different depths in boreholes at the Eolian Mantle
- Sampling of rain water, surface water and groundwater at different depths (springs, water table boreholes, nested boreholes, agr. wells):

- Chemical data: Cl, SO₄, HCO₃, NO₃, Na, K, Ca, Mg, NH₄, NO₂, PO₄, Fe, Mn, Br (1992-2009, some 850 samples)
- Isotopic data: ¹⁸O_{H2O}, ²H_{H2O} (1990-2007, 480 samples)
³H (1990-2005, 384 samples)
¹⁸O_{SO4}, ³⁴S_{SO4} (2002-2007, 60 samples)
¹³C_{DIC} (1990-2007, 25 samples)
¹⁵N_{NO3}, ¹⁸O_{NO3} (2007-2009, 21 samples)

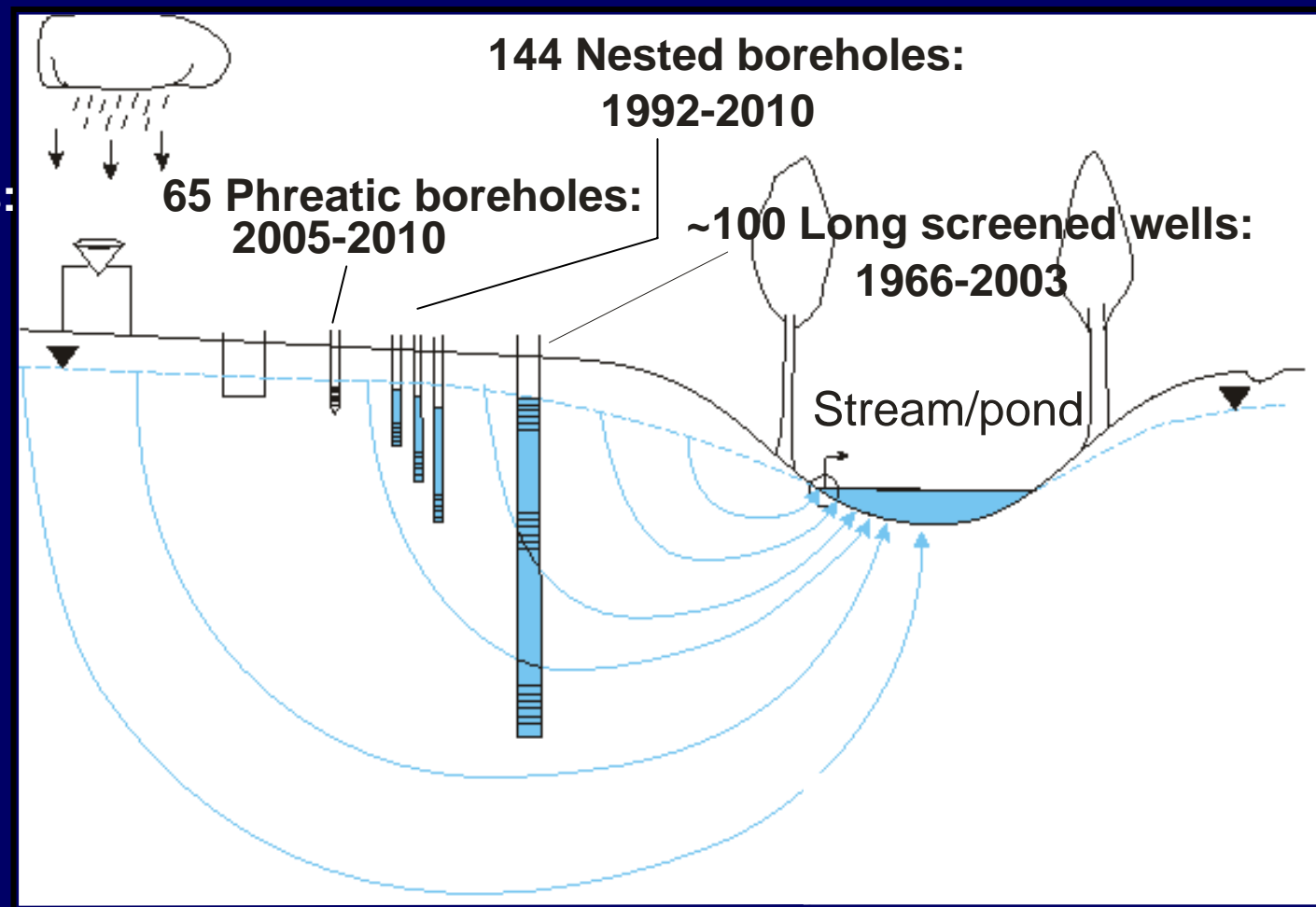
METHODS

- Groundwater flow modelling (MODFLOW and Visual Transin, UPC)
- Characterization of solute sources (atmospheric, lithologic, manure)
- Characterization of hydrogeochemical processes during recharge and along GW flow
- Hydrogeochemical modelling (PHREEQC)

2. Materials and methods

- Types of sampling points and recording periods:

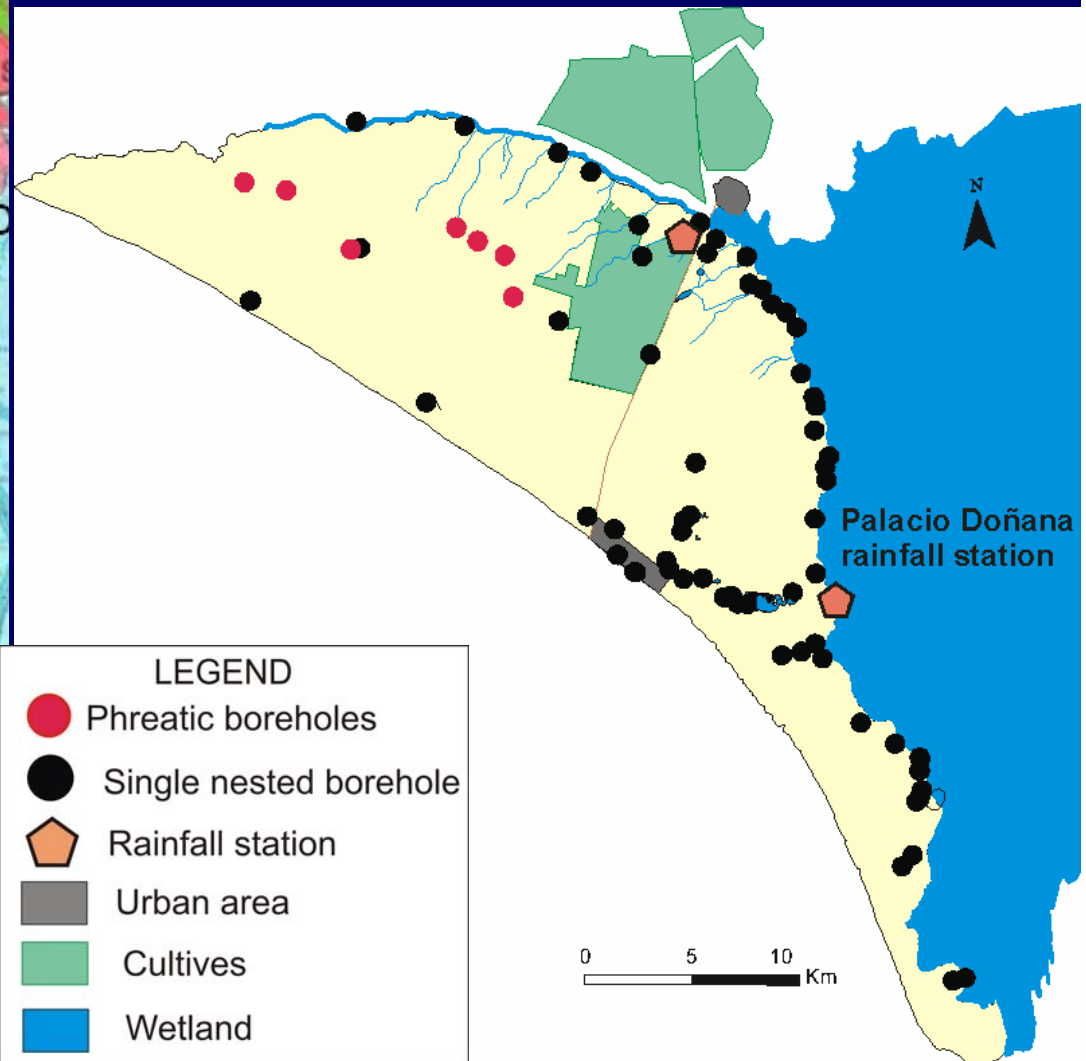
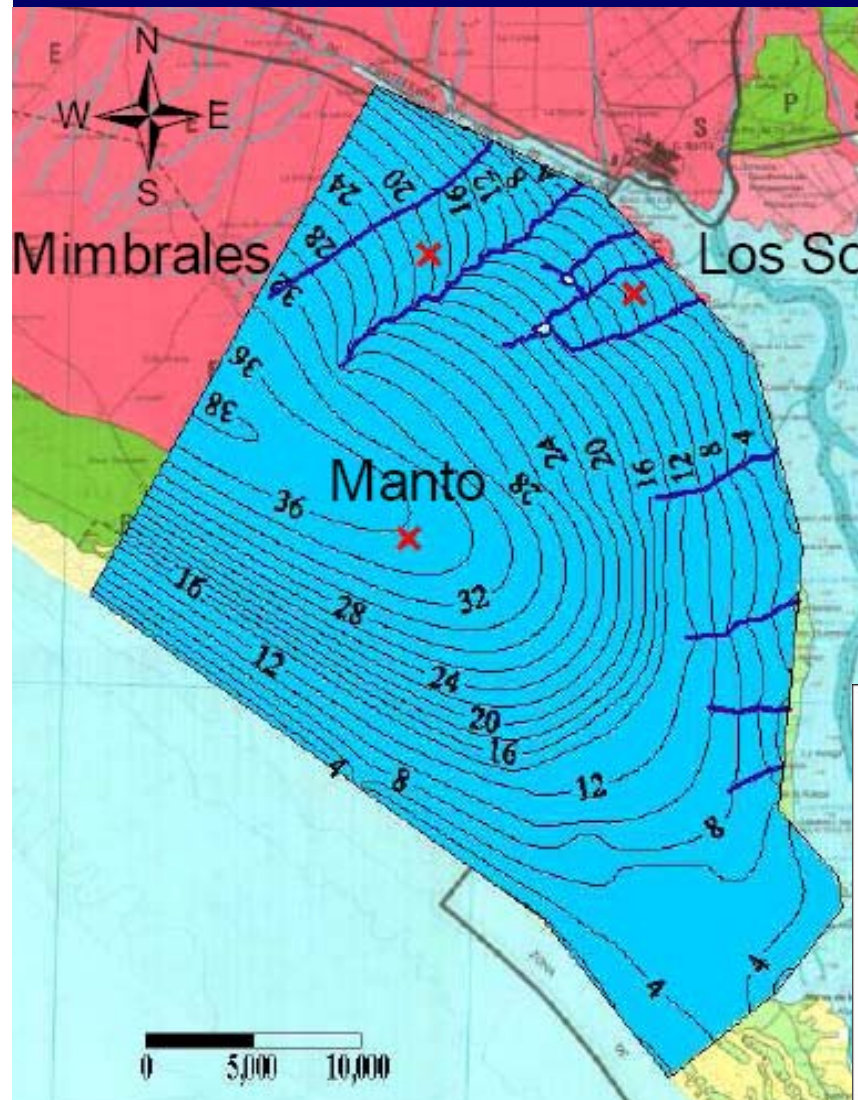
**2 Rain stations:
2007-2010**



3. Groundwater flow modification due to abstractions

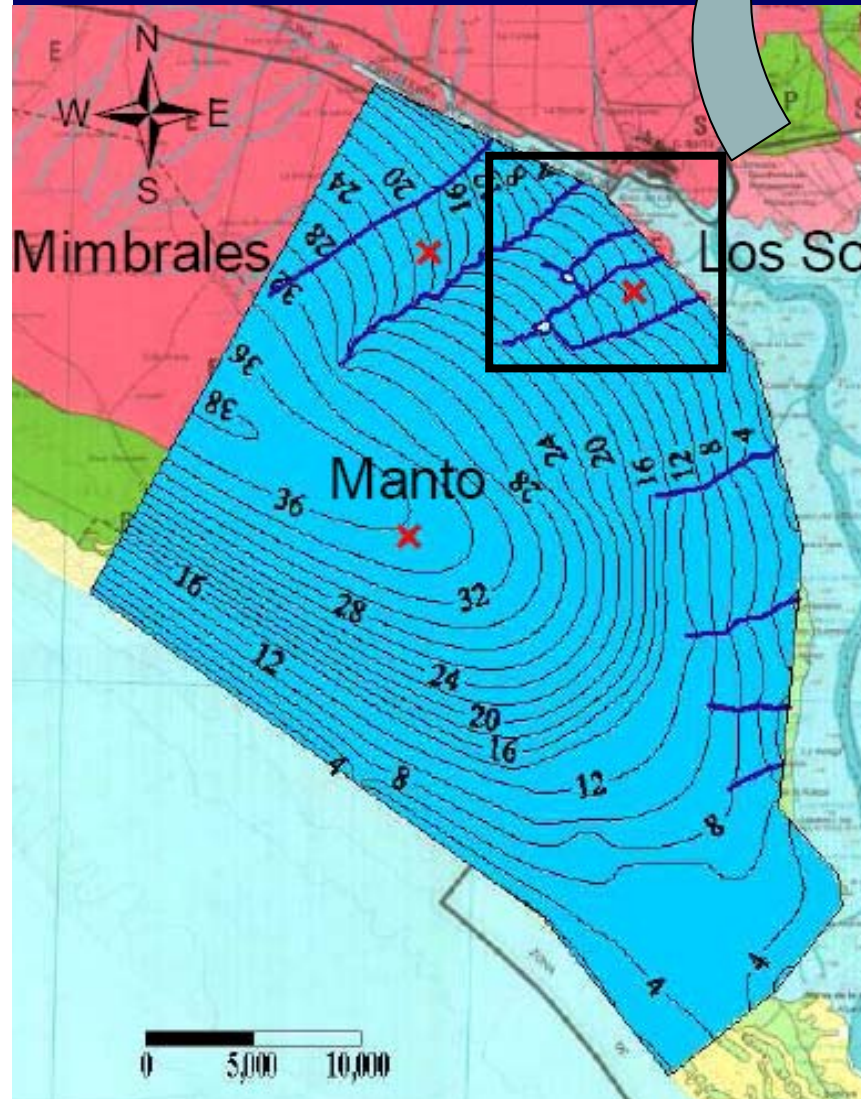
Natural flow conditions

Under natural conditions most of the streams and ponds were discharge areas

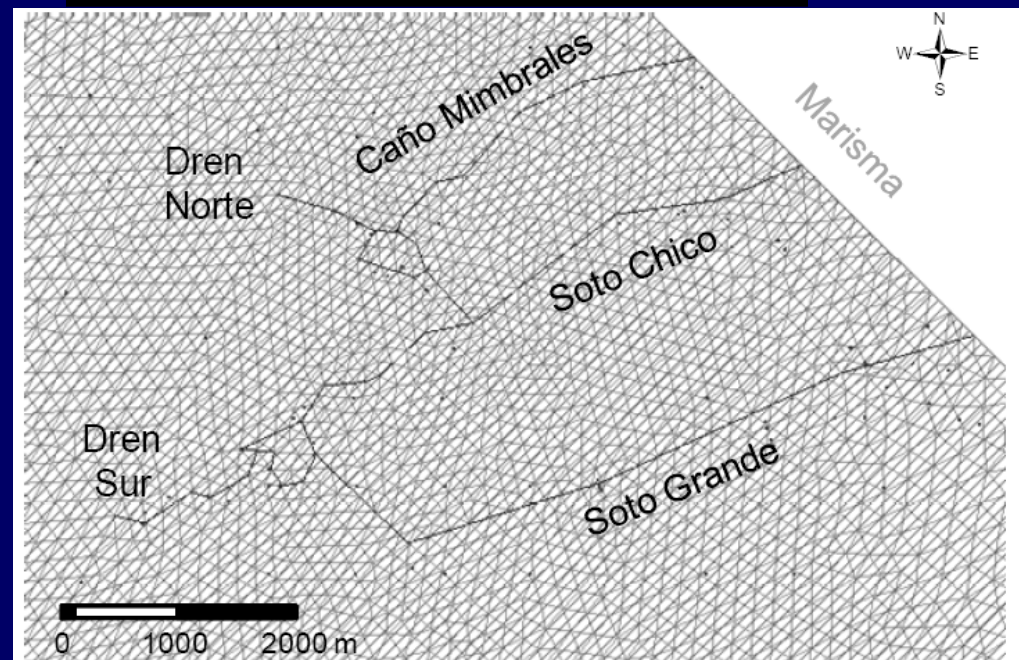
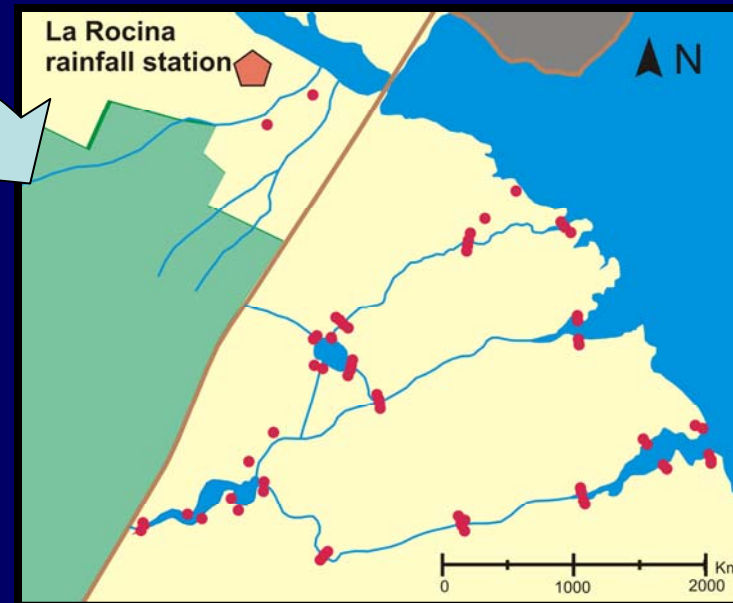


3. Groundwater flow modification due to abstractions

Natural flow conditions

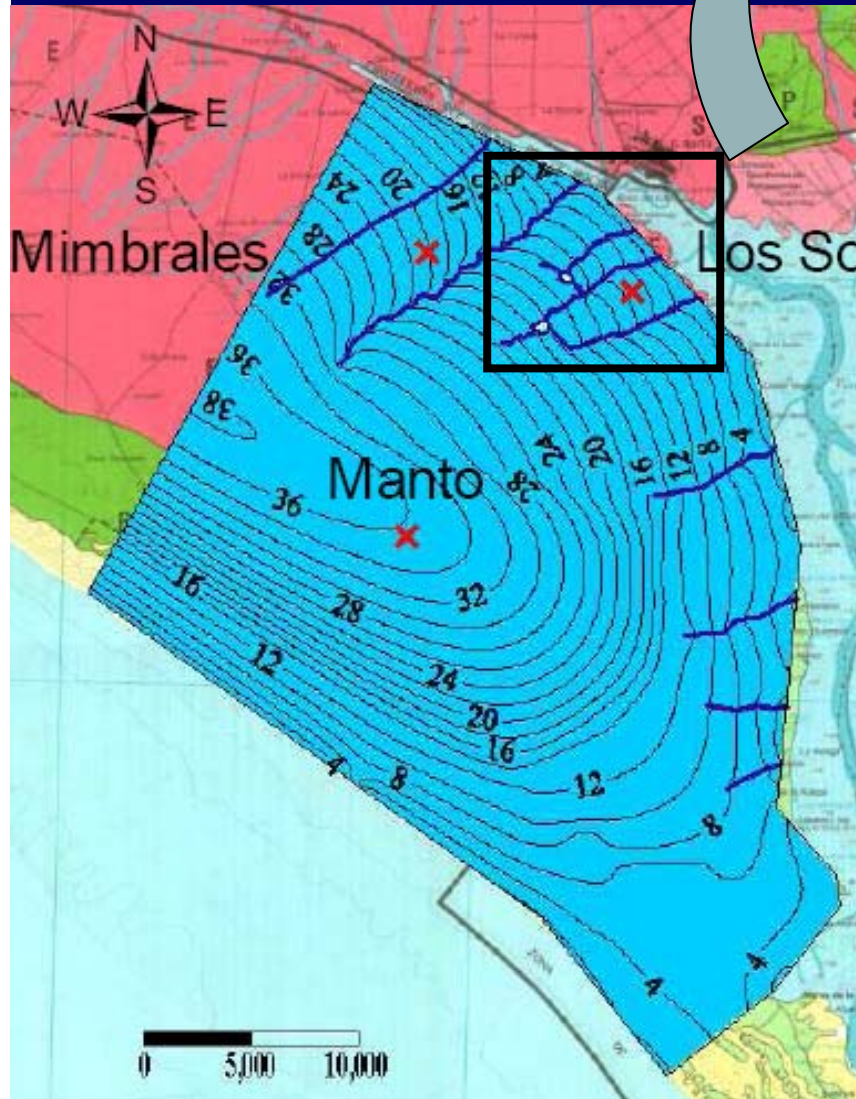


Influenced conditions



3. Groundwater flow modification due to abstractions

Natural flow conditions



Influenced conditions



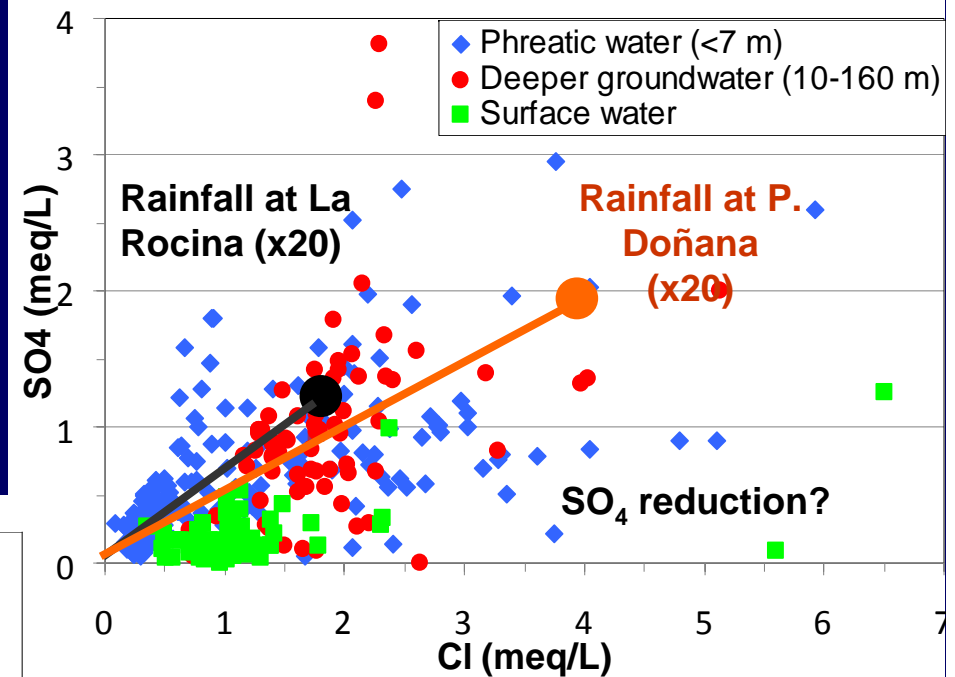
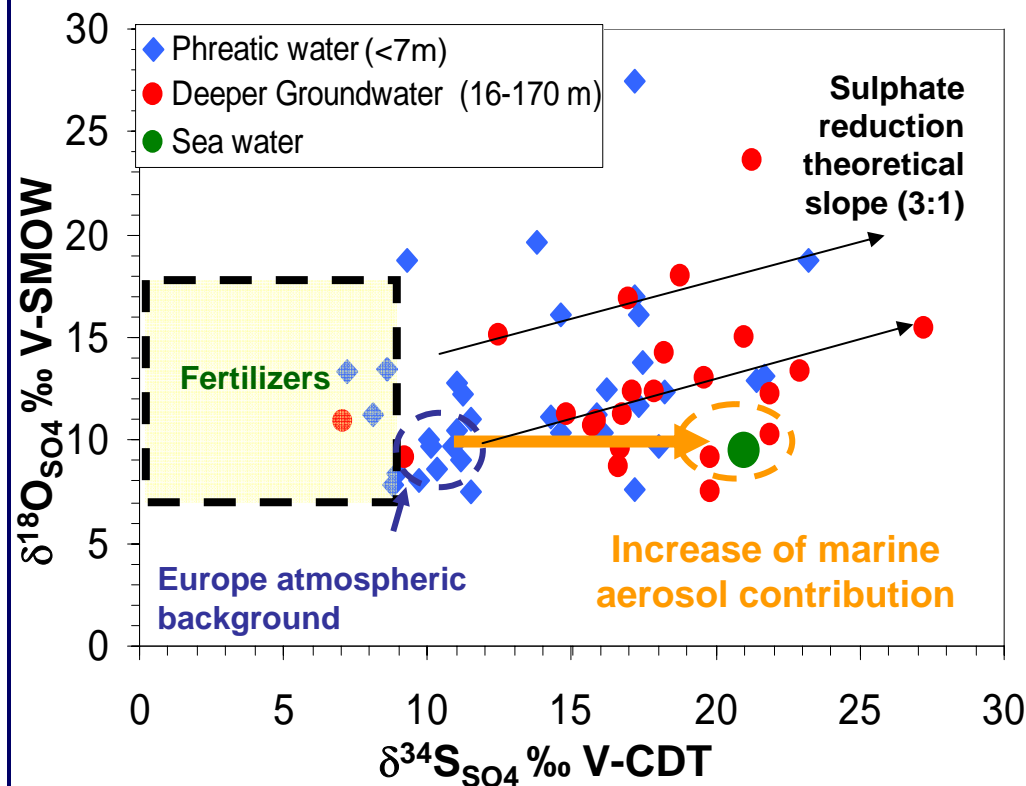
Under influenced conditions most of the streams and ponds are disconnected to the water table.

Thus, part of the former natural discharge to streams and ponds is nowadays pumped.

4. Hydrochemical impact of agriculture. Input and fate of S+N

■ Sources of S

- Atmospheric input (wet + dry deposition).
- Other. Hypothesis:
 - * Fertilizers (from nearby fields)
 - * No mineral sources for S



■ Results

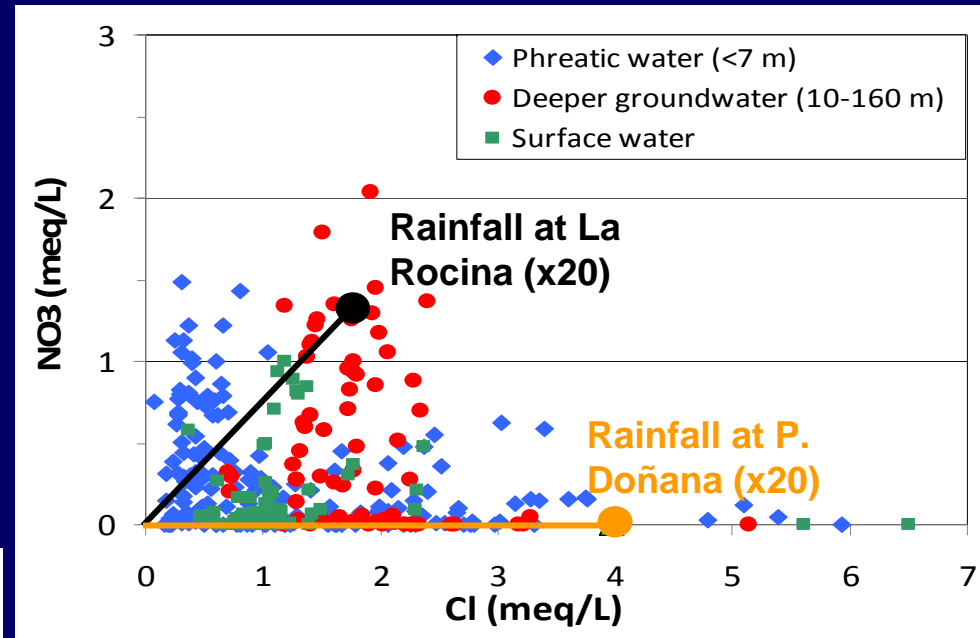
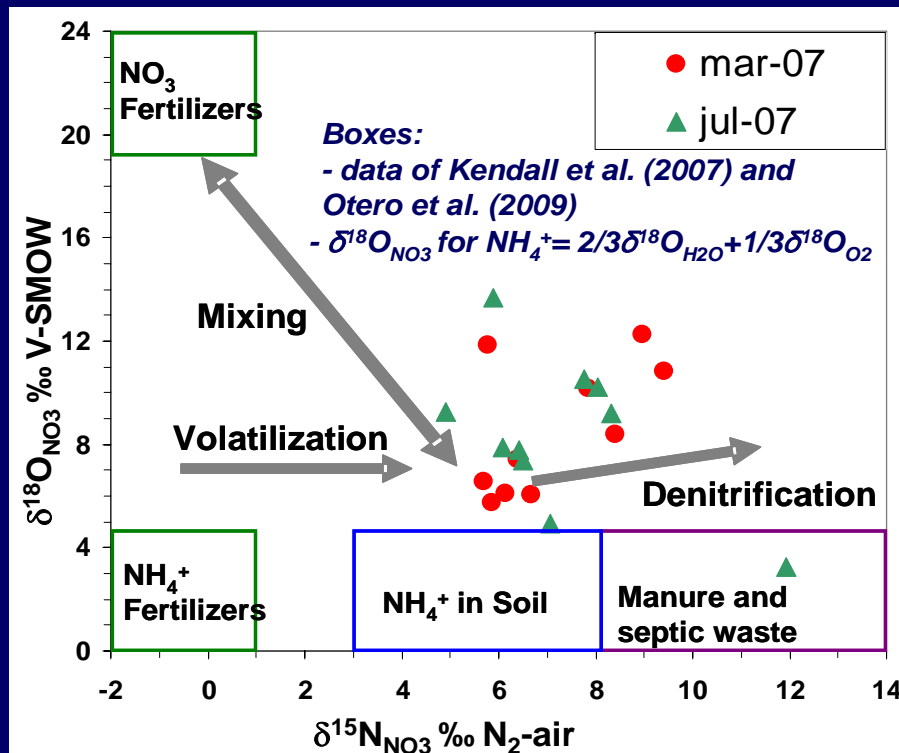
Contribution of agrochemicals seems clear in some samples.

Reduction processes take place.

4. Hydrochemical impact of agriculture. Input and fate of S+N

■ Sources of N

- Atmospheric input (high NO_3 content in some rain samples at La Rocina).
- Other. Hypothesis:
 - * Livestock manure
 - * Fertilizers (from nearby fields)
 - * Soil organic matter (small)



■ Results

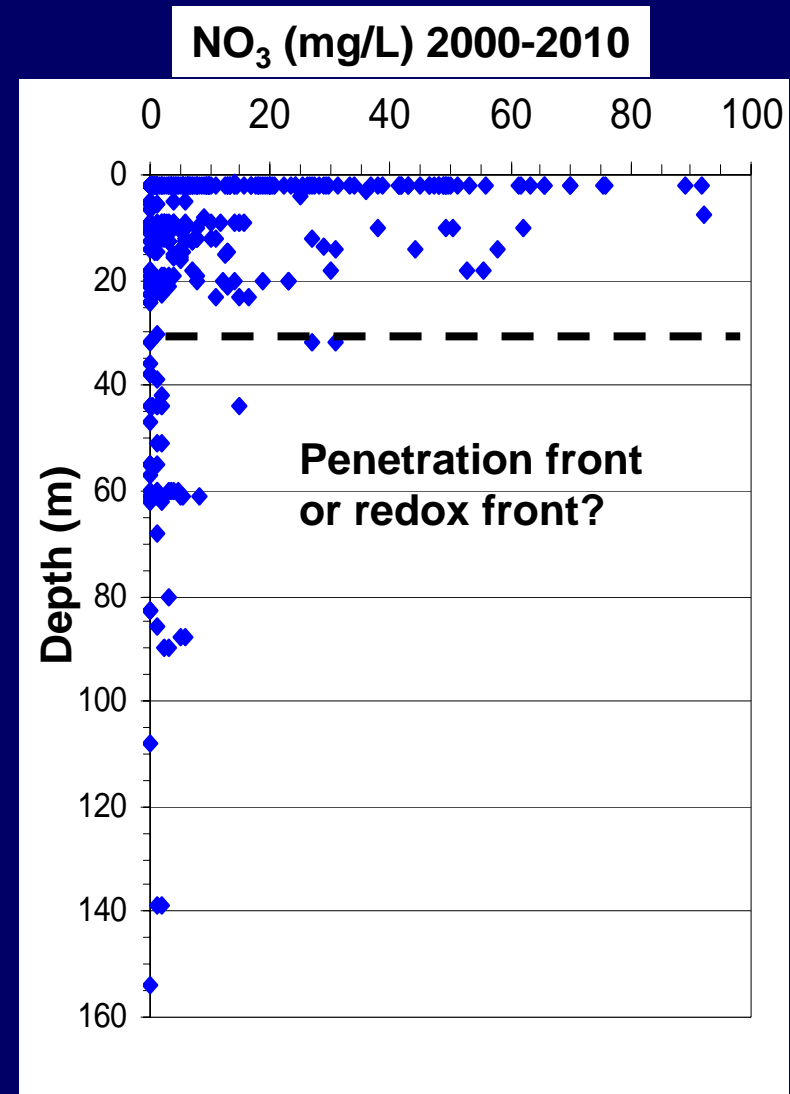
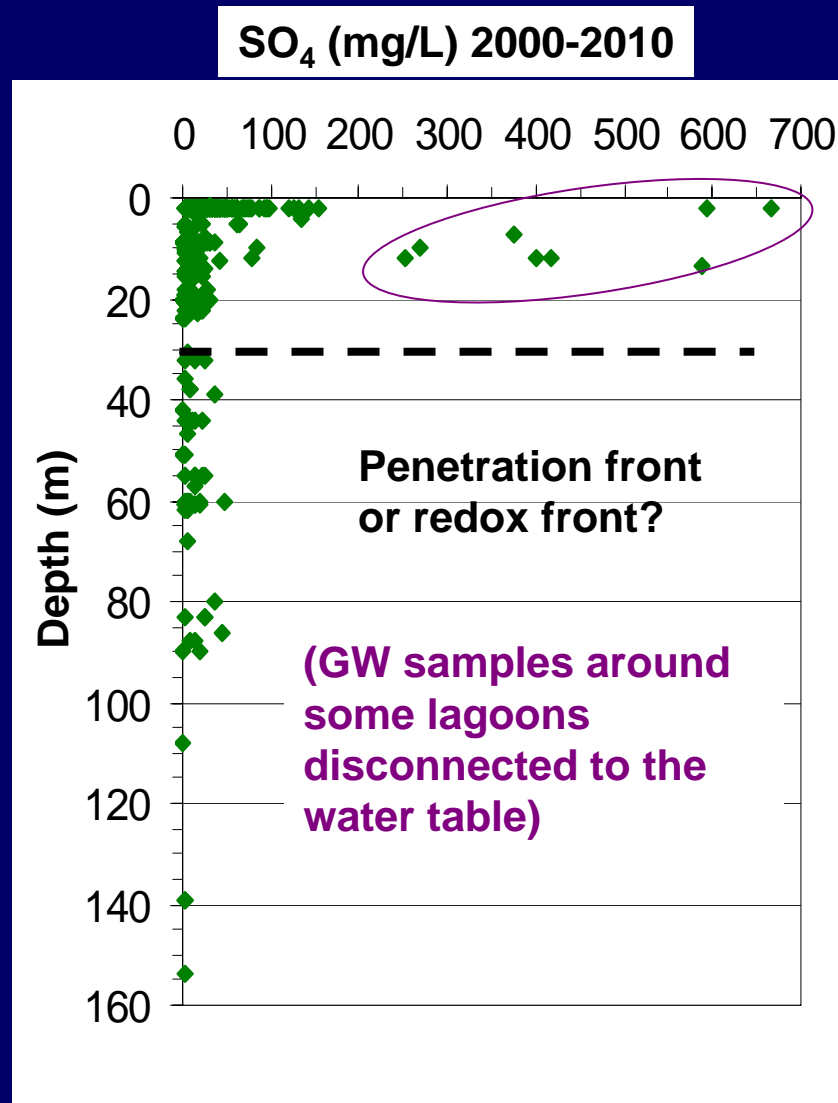
Isotopic contents compatible with oxidation of ammonium from fertilizers (probably after N volatilized during fertilization).

Some contribution from soil and from cattle manure can not be discarded (and is under study).

NO_3 reduction processes not clearly seen, but not discarded.

4. Hydrochemical impact of agriculture. Input and fate of S+N

■ Modification processes with depth in the aquifer (1)

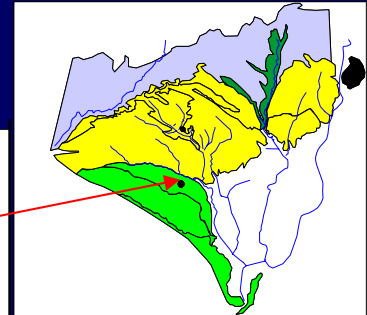
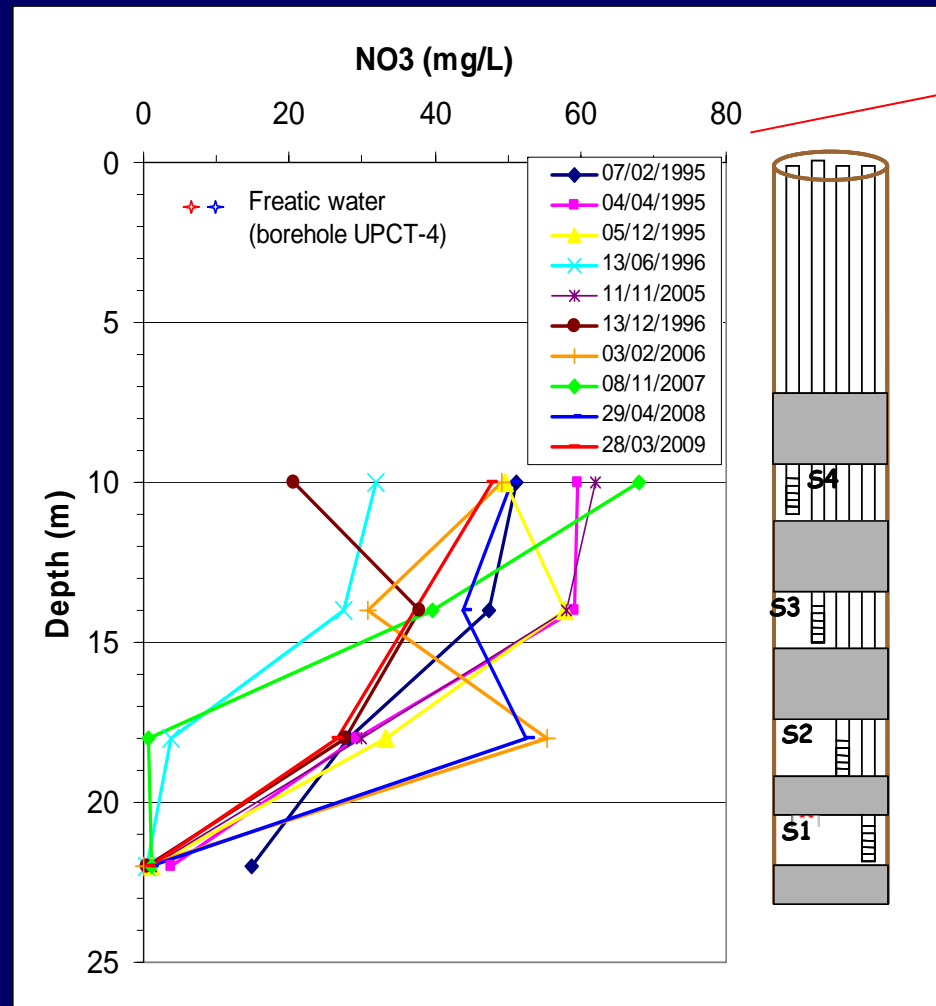


4. Hydrochemical impact of agriculture. Input and fate of S+N

■ Modification processes with depth in the aquifer (2)

El Tejar Farmland:

- Cultivation ended in 2000.
- N remaining in the soil was expected to be observed moving downwards in next years, but it did not happen.
- This support the hypothesis of reduction processes at around 25-30 m depth.



5. Main conclusions

1. In large areas of the Doñana Eolian Mantle aquifer sector, the GW natural pattern and the solute sources have been modified by the management of soil and water.
2. Intensive aquifer exploitation from early 1970 has led to piezometric (and water table) drawdown, which induced disconnection of some wetlands from active groundwater flow.
3. Isotopic data point to atmospheric supply and fertilizers as the sources for S in the aquifer.
4. SO_4 reduction processes take place in the area surrounding some wetlands, and also at around 30 m in the aquifer, suggesting a reduction front at this depth.
5. The main source of N seem to be fertilizers, but reaching GW through oxidation of volatile N species. However, manure from the abundant cattle wandering through the area can not be discarded as a complementary source (under study).
6. NO_3 reduction processes seem to occur at around 20-25 m in the aquifer, supporting the hypothesis of a reduction front at this depth.

Acknowledgements

- International Atomic Energy Agency, CRP project *“Isotopic Techniques for Assessment of Hydrological Processes in Wetlands”* (2007-2010).
- Spanish Ministry of Environment project “Doñana 2005”, Research *“Impact of Actuation # 1 on the relationships between wetlands and the aquifer”* (2005-2009).