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## **Extended Abstracts**

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Groundwater contamination — monitoring, risk assessment and restoration

title: Hydrogeological study of contamination in the Aquifer System of Sines, South Portugal

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#### INTRODUCTION

The Aquifer System of Sines is located in the western coast of South Portugal (Figure 1), and it is formed by sedimentary rocks overlying the Paleozoic metamorphic rocks of the South Portuguese Zone. It is a complex aquifer system, mainly composed by two aquifers, the top one phreatic, porous, built by tertiary sands interbeded with more clayish formations, and the second one confined, composed mainly by limestones, with mixed karstic and porous characteristics. In the south part of the system the geology is more complex, influenced by the intrusion of an igneous batholith south of the aquifer, accompanied by radial dykes, which disrupt and disturbed this part of the aquifer. In this area the upper and the second aquifer are sometimes linked, sometimes interrupted by tectonics, with an extreme variance not so easy to understand.

In the nineteen seventies, some industries based in oil products were installed and have started activity in the south part of the system (Fig. 1).



**Figure 1.** The Aquifer System of Sines (inside the blue line), in the western cost of South Portugal. All groundwater in this aquifer system flows essentially from east to west, in direction to the sea. In the shaded area of the south part of the system (east of Sines) an industrial area was installed in the seventies, including a refinery and other industries based in oil resources. Two main well fields guarantee the supply of potable water to the population and the industrial area, being the south one immediately downstream of the industrial area (ICCE 2009).

The expansion of some urban areas (in the city of Sines) and the creation of an entire new city (Santo André) to accommodate the workers for the new industrial area, led to an increase on the demand of quality water for the public supply system, including potable water for the industrial area. This supply has been based in groundwater from this aquifer system. The water for industrial processing was based in an artificial lake created by the construction of a dam nearby the city of Sines, using water transference from another river east of Sines, the Sado River. Two abstraction areas were created. The northern one is based in the confined aquifer, near the city

of Santo André (Santo André Well Field in Figure 1), where this aquifer is protected by impermeable clay and limestone compact layers, at about 60 to 80 m deep. Here the wells are artesian and can have more than 100 l/s of flow as natural discharge at surface. Most part of these wells allows the abstraction without the need of pumping, using only the natural discharge. These wells supply the city of Santo André, the industrial area of Sines, and Sines municipality in summer, when a high quantity of tourists come to this coast on vacations and there is the need to strengthen the Sines supply system in drinkable water. In the south part of the aquifer, northeast of the city of Sines, other group of wells (Sines Well Field in Figure 1) supplies water to this city, with exception to the industrial area, supported by the first set of wells. These non artesian wells were drilled in the border of the industrial area, downstream the aquifer flow, and, in 2009, some analysis showed the presence of hydrocarbons in groundwater. At the same time, contaminated soils were identified inside the industrial perimeter.

#### **GEOLOGY AND HYDROGEOLOGY**

The sedimentary infill of the Meso-Cenozoic intracratonic Sines basin (Figure 2), supporting the multilayer Sines Aquifer, reaches a thickness of more than 1,000 m.



**Figure 2.** Schematic approach to the geology of the area of the Aquifer System of Sines. The aquifer system is delimited by the black line. East of Deixa-o-Resto and Santo André a fault (Deixa-o-Resto Fault) marks the recharge area of the confined karstic aquifer. West of this fault, the limestones that outcrop in contact with the fault on its eastern border are at 60 to 80 m deep, defining the eastern border on the confined aquifer, which extends to the coast and, probably, by some hundred meters under the sea.

The basin contacts with low permeability Carboniferous flysch turbidites to the South and to the East and with the sub-volcanic Sines massif to Southwest. The Grândola Fault defines the northern boundary of the sedimentary basin. The oldest sediments in the Sines Basin consist mainly of red continental sandstones and mudstones (Silves Formation). Above this Triassic siliciclastic rocks, with an average thickness from 80 to 120 m, a sequence of Hettangian-

Rhaetian evaporites, clay and marls (80 m) and dolomites (15-40 m) were deposited. Sinemurian-Hettangian deposits (130 m) are dominated by marls, clays, dolostones and limestones intruded by basaltic and doleritic dikes and are followed by the Jurassic carbonate rocks, supporting the most important and deeper regional aquifer of the basin, which is artesian in an important part of its area. The sequence of these carbonate rocks starts by Early Jurassic (Toarcian-Sinemurian) limestones, dolostones and marls (100 m). It is followed by Middle Jurassic (Callovian-Bathonian) limestones (250 m) and finishes with 600 m of Late Jurassic limestones, marls and conglomerates (Oxfordian-Kimmeridgian). Due to the absence of Cretaceous rocks (except for the off-shore part of the basin, where sediments of this age were identified) the Miocene deposits follow the Jurassic rocks in the sedimentary sequence (Inverno et al., 1993). Outcrops of Miocene lithologies are scarce in the Sines Basin and are represented by sands, silts, sandstones and biocalcarenites. The thickness of the Miocene deposits is in the order of 30 m and was identified in boreholes under Plio-Pleistocene and Holocene deposits, at a depth varying between 8 m and 40 m (Oliveira et al., 1984). The Plio-Pleistocene silt and clay sands, together with beach and dune sands are the most important deposits covering the Jurassic rocks. These detritic rocks are present in the western coastal plain, which is limited by the ocean to the West and by the Santiago do Cacém Hills (with an altitude between 50 and 200 masl) to the East. These hills, built by early and middle Jurassic carbonate rocks outcrops, define the limit of the Mesozoic formations of the Sines Basin and form the main recharge area of the deep carbonate aquifer. The area with outcrops of late Jurassic carbonate rocks is very limited. These rocks occur in the coastal plain, covered in most of its area by the Miocene, Plio-Pleistocene and Holocene sediments. The Holocene deposits, associated with lowlands at the Melides (0.4 km<sup>2</sup>), Santo André (2.5 km<sup>2</sup>) and Sancha (0.2 km<sup>2</sup>) lagoons were deposited in the terminal reaches of the Melides, Ponte, Badoca and Sancha creeks. These deposits consist essentially of detritic, minerogenic and organic sediments arranged in several units with a maximum thickness of about 40 m (Freitas et al., 2002). These deposits limit the hydraulic connection between the lagoons and the shallow detritic aquifer, due to the fine fraction of the sediments in the lagoons. However, as the rivers associated with the shallow lagoons aquifer are effluent in the terminal reaches, where sediments are coarser than in the bottom of the lagoons, the water balance of the lagoons is controlled by the hydraulic connection of the stream network with the shallow aquifer. Figure 3 shows the geological and hydrogeological profile of this aquifer.



Figure 3. Geologic and hydrogeologic west-east profiles of the area of the aquifer system of Sines, in the area of Santo André (Oliveira 1984, Esteves Costa 1994, respectively).

#### ACTUAL GROUNDWATER USES IN THE AQUIFER SYSTEM OF SINES

The aquifer system of Sines is mainly composed by two aquifers, a porous phreatic one on the top, in the first 60 m, and a karstic one, confined, under 70–80 m deep in the western part of the fault of Deixa-o-Resto. The bottom of the second one is unknown, but the limestones are known to be on the order of several hundreds of meters. Recent drillings in this aquifer showed what seems to be a karstic system filled with sand and a great quantity of fossils.

As it can be seen in Figure 1, this aquifer system presents two main pumping fields, one responsibility of the private company Águas de Santo André, SA (the northern one) and the other responsibility of the Municipality of Sines (the south one). The first field is supported by wells in the karstic confined aquifer, varying between 100 and more than 200 m deep, and all the supply wells are artesian, with natural flow at surface varying between 30 and 110 l/s. The second field is situated in the south part of the system, where the aquifer is not so well defined, due to the intrusion of the magmatic rocks in the area of Sines during the Alpine Orogeny; in this area both the phreatic and the confined aquifers are surely linked in some areas, but they can also be independent on others, and there is no more signs of artesian flow in the area. One strong possibility, due to the deficient construction of the wells of the Sines Well Field (for example there are no signs in some of the wells of any vertical protection, the tubes were just inserted into the well, but the flow cross all the layers outside the casing), is that the wells can be responsible by the flow by-pass between the two aquifers.

Recent studies (Chambel, Monteiro 2007; Monteiro et al., 2008) showed that the abstraction rates in the confined aquifer must be about 50% of the infiltration rates. From this 50%, 5% are supposed to be abstracted from the infiltration area of the confined aquifer and used mainly in agriculture, and 45% are justified by these two well fields and some private wells used inside the industrial park. So, from a total average infiltration of  $12 \times 10^6$  m<sup>3</sup>year<sup>-1</sup>, a calculated value of  $6 \times 10^6$  m<sup>3</sup>year<sup>-1</sup> is abstracted in the confined aquifer.

#### CONTAMINATION

In the southern well field (Sines Well Field) some hydrocarbon contamination had begun to be detected in analysis since 2009. The wells are down flow the industrial area, involving at least two oil industries in its vicinity, one at south-east, and other north-east of the well field. The global analysis of data shows that the presence of hydrocarbons is increasing along the months, namely the naphthalene and total oil hydrocarbons. From all the detected polycyclic aromatic hydrocarbons (PAH's), the presence of naphthalene is the only one which clearly results from industrial synthesis; all the others are present in bitumen as well in other organic materials. So, the naphthalene can clearly help to identify industrial origins, opposing natural origins. Even so, the PAH's are present in concentrations less than admitted by the Portuguese law and international directives, so the contamination levels are not yet dangerous, but of high concern, due to the fact that the place is just outside an industrial area. Also the presence of xylene, with quantities that had passed 25 times the levels defined by the 'Dutch List' (VROM, 2000) in some analysis, are compatible with contamination based in oil derivates. The presence of naphthalene, BTEX (in this case only the case of xylene) and hydrocarbons of oil clearly indicate the presence of anthropogenic contamination.

The substances originated from human activities can accommodate in the following origins:

- Migration from industrial origins nearby,
- Groundwater migration from landfills of chemical substances nearby,
- Groundwater migration coming from pipelines with chemical products,
- Nearby wells with deficient protection permitting the contamination between aquifers,
- Contamination through surface in wells without upper protection against vandalism or accidental spreading of substances.

#### CONCLUSIONS

The detection of hydrocarbon contamination in the aquifer system of Sines had led to three basic actions: the decontamination of contaminated soils, a deep study of the aquifer contamination (flow patterns, attenuation, degradation, diffusion or miscibility processes of pollutants), and a geophysical study to implement new supply wells for the city of Sines. A new inventory of wells and contamination points was developed and a new piezometric map was defined for the aquifer system. The evolution of contaminants has been followed and remediation measures will be proposed if it shows essential for the protection of the groundwater resources. Isotopic studies are planned, in order to help understand the water time travel from recharge to discharge areas.

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