Arsenic source and release process in a coastal wetland located in the south eastern Po plain (Italy)

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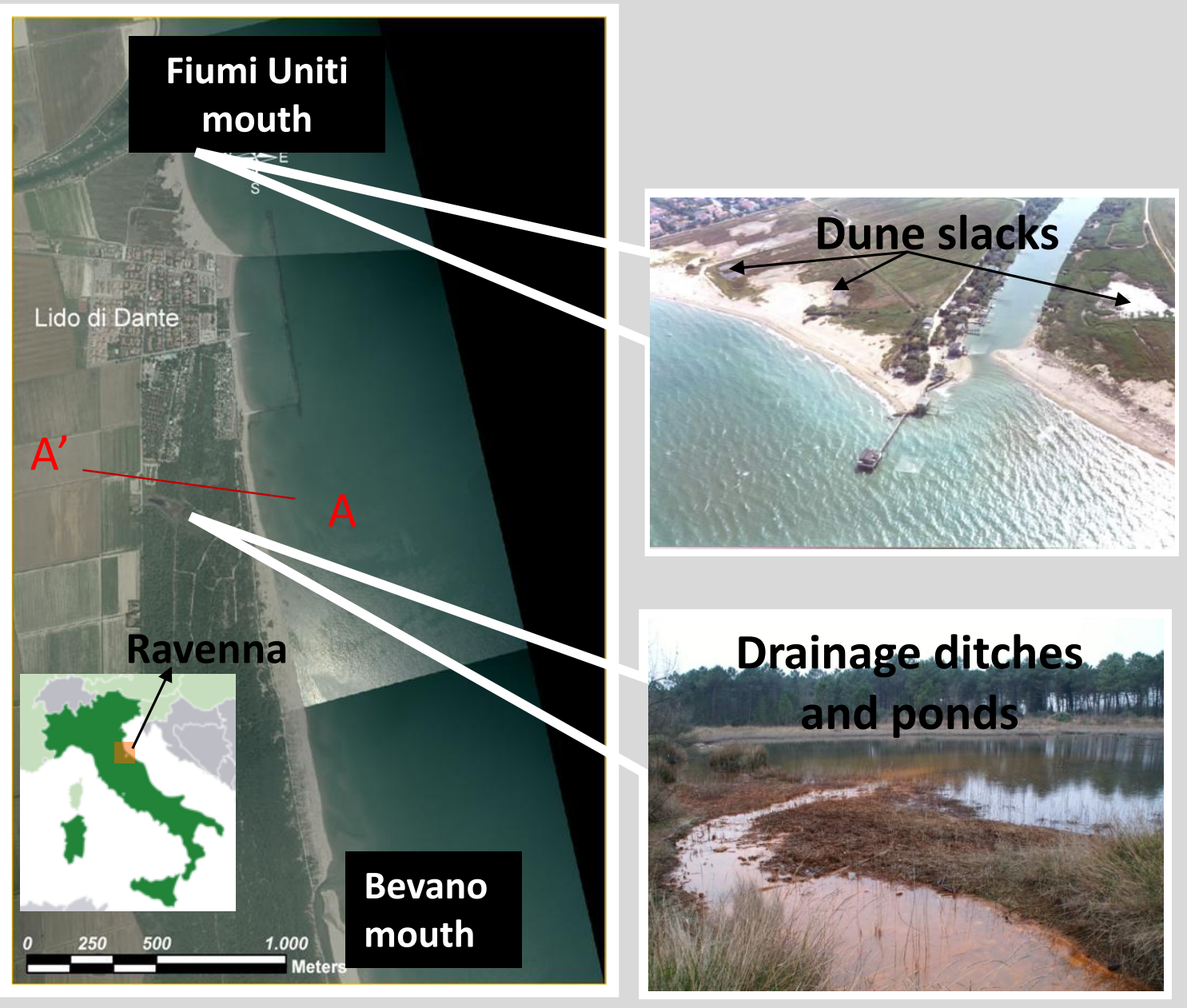
Introduction

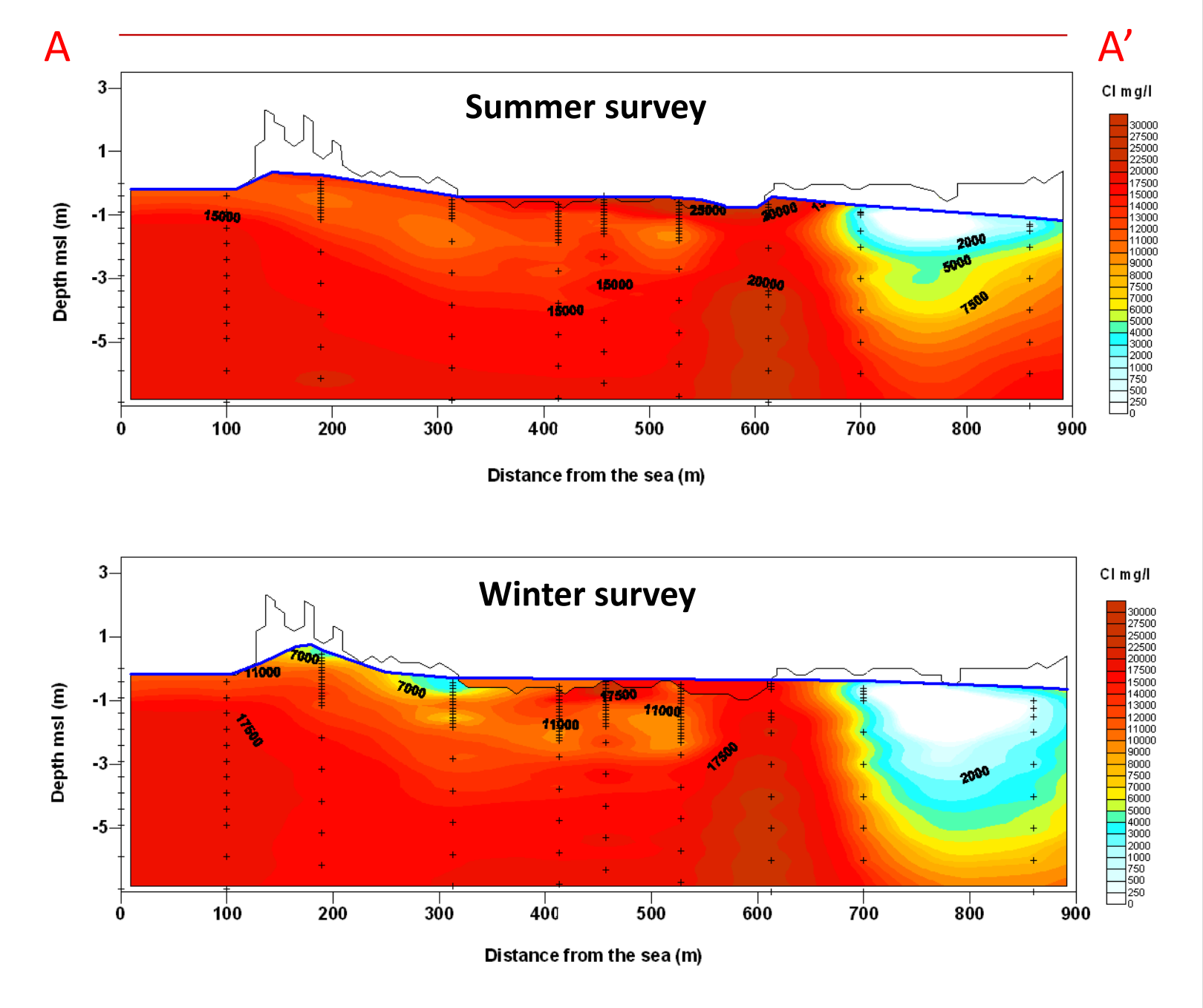
We studied the hydrogeochemistry of the phreatic aquifer in the coastal area included between Uniti and Bevano rivers (southern part of the Po plain, near the city of Ravenna). Arsenic is a natural pollutant of these waters : a regional Arsenic anomaly is well known in deeper groundwater (in the range 50 - 100 µg/l, according to Farina et al., 2005).
High As concentrations in the confined aquifers of Ravenna are supposed to be due to Fe hydroxide dissolution, which can be caused by redox potential fluctuations (Ravenscroft *et al*., 2009; Marcaccio *et al*., 2005).
This study is one of the first attempts in the area to characterize the hydrogeochemistry of the shallow groundwater system and to investigate on the distribution of As within the phreatic aquifer.
During four seasonal monitoring survey in the study area, we collected 94 samples of groundwater and surface water. Arsenic concentrations were measured with hydride generation methods for the ICP (inductively coupled plasma). The method is based on the reaction of As (III) with Sodium-Boron hydride to obtain the arsenic hydride (APAT, 2003).
We also analysed soil samples , which were collected at three different dephts ranging from top soil (0-0.05 m from filed level) to the interface between the unsaturated zone and aquifer (0.7-0.8 m fro field level).

Study area



The coastal part of the Po plain consists of a low-lying and mechanically-drained farmland further from the sea and of a narrow belt of dunes and pine forests in the backshore area . The water table level is lying close to the land surface and surface water is present as dune slacks, ponds, drainage channels and rivers. Most of these water bodies are located into depressions and are directly linked to the groundwater, as the top layer is sandy in all the study area except for the northern part (close to the Fiumi Uniti river mouth), where the top layer is made of clay Surface water bodies are characterized by iron hydroxides precipitation, which result in a thin extensive layer at the bottom of ponds and ditches. Iron hydroxides are also present as in the sandy sediments of the unsaturated zone as thin horizons located in the water table fluctuations interval.

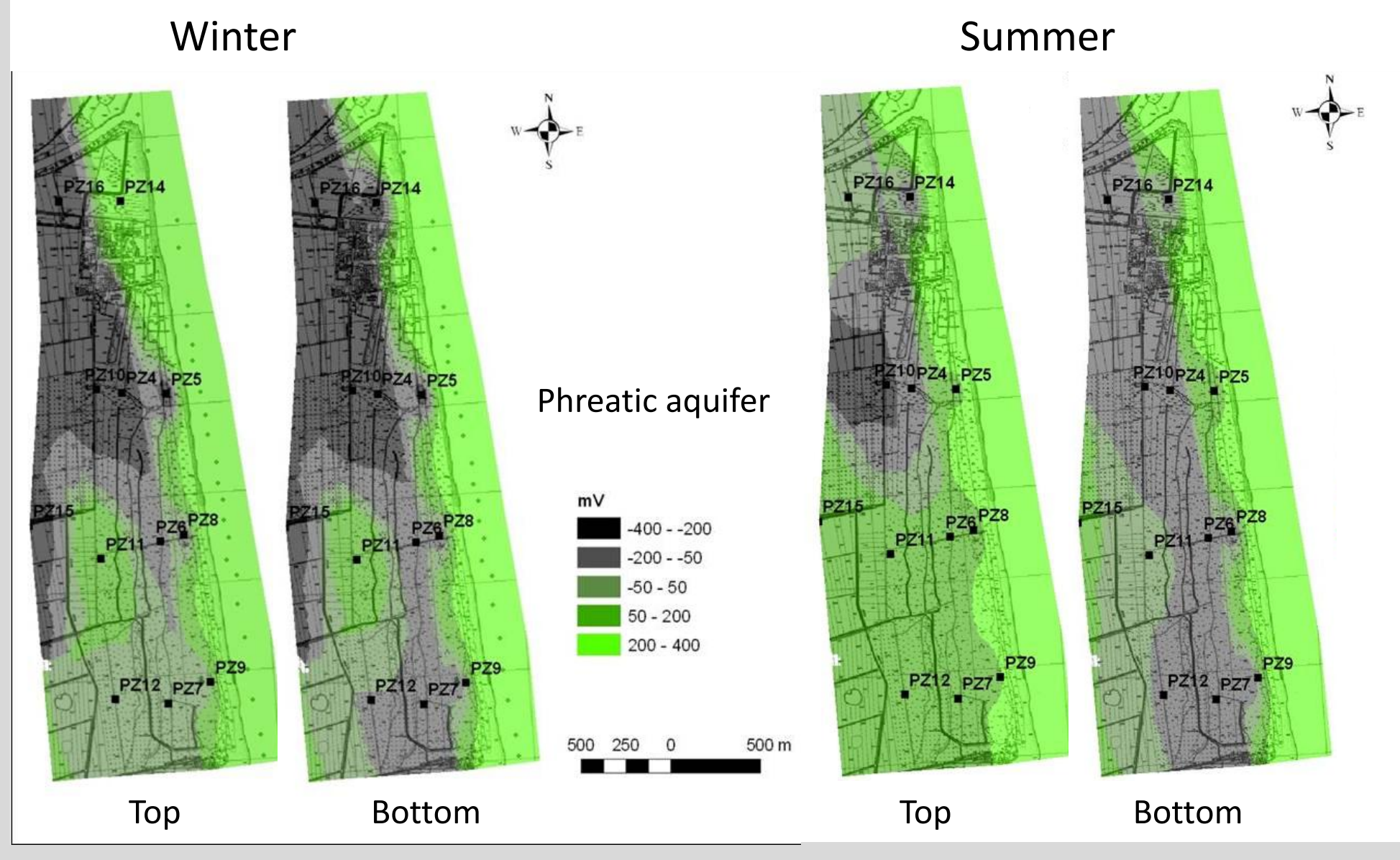
As a result of an intensive exploitation of coastal aquifers for agricultural, industrial, and civil uses, both the phreatic aquifer and the surface waters (drainage ditches, ponds and dune slacks) have been contaminated by seawater and by deeper groundwater. The upconing of deep groundwater in ponds and ditches has been detected mapping the Chloride distribution in several 2D profiles in the study area (Marconi et al. 2010).



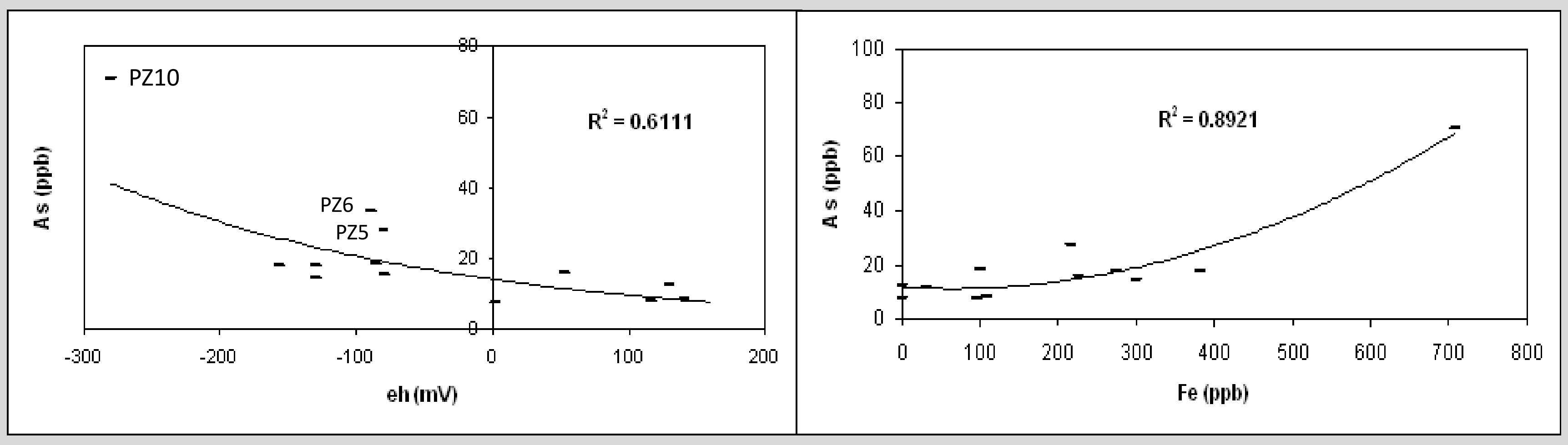
In the summer a severe surface water evaporation is taking place in the pond, located in the backshore area. During this season the pond is partially dry: salts and organic matter precipitates at the bottom of the surface water body.
Deep chloride-rich groundwater is seeping in the lowest side of the pond, where the phreatic level is below sea level. Top, fresher groundwater discharges from the dunes belt towards the pond, where a mixing with the hypersaline pond water occurs.
The seepage of salt deeper groundwater is taking place into the lowest side of the pond in both the monitoring seasons.

Arsenic release

The crystal lattice of Fe hydroxides has the capability of adsorbing Arsenic and it is easily altered by the redox potential changes: crystal lattice alterations induce As release (Martinelli et al., 2005). Redox variations may occur after water-table fluctuations due to water pumping in deep aquifers and to evapotranspiration, rainwater recharge and mechanic drainage in the phreatic aquifer.
In shallow environments the Arsenic release is limited with respect to groundwater (Scialoja et al., 2005).
Arsenic mobility is maximum in the typical range of groundwater pH values 6.5-8.5: As-anions are soluble in neutral waters, as it is for several chemically related elements such as Cr, U and Se. Between these elements, As behavior is marked by its still great mobility at negative redox potential conditions (Bissen & Frimmel, 2003).
Recent studies evidenced the role of Arsenic–reducing bacteria in the As transport and speciation in the hyporeic zone (Oremland & Stoltz, 2003).
The picture shows the observation wells network (black dots), which has been used for monitoring the water quality in the phreatic aquifer. The wells are fully screened and water samples have been collected by means of a multilevel sampler.

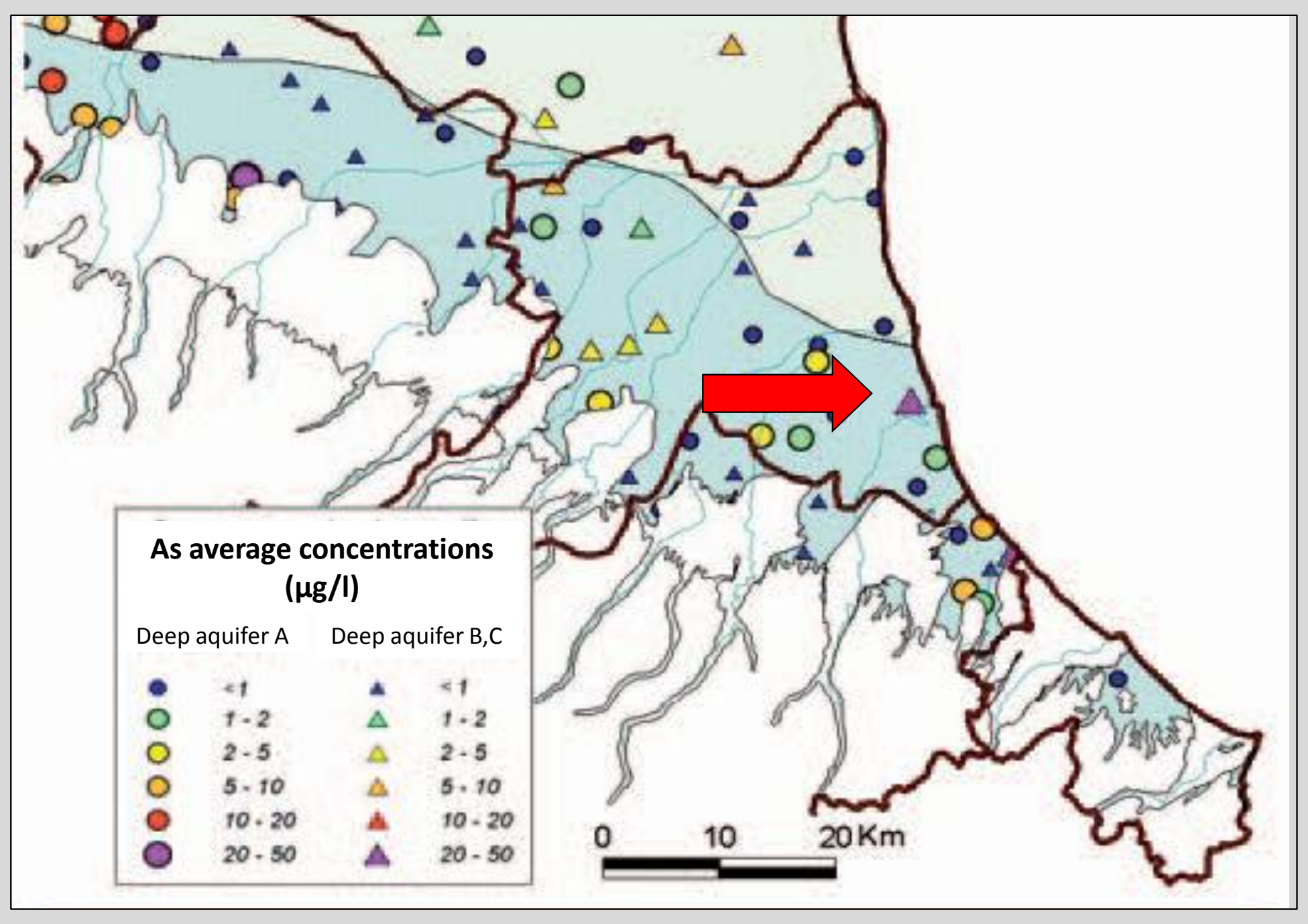


The redox potential distribution was measured at the top and at the bottom of the groundwater. In both the summer and winter seasons. The resulting maps indicate that the redox potential is negative in the proximity of ponds and dune slacks, which are located in the northern side of the study area. In the winter survey the values of this parameter are practically identical at the top and at the bottom of the aquifer, whereas there is more variability in the summer.
On the contrary, pH values are very uniform in space and time and are always included in the range of neutrality.



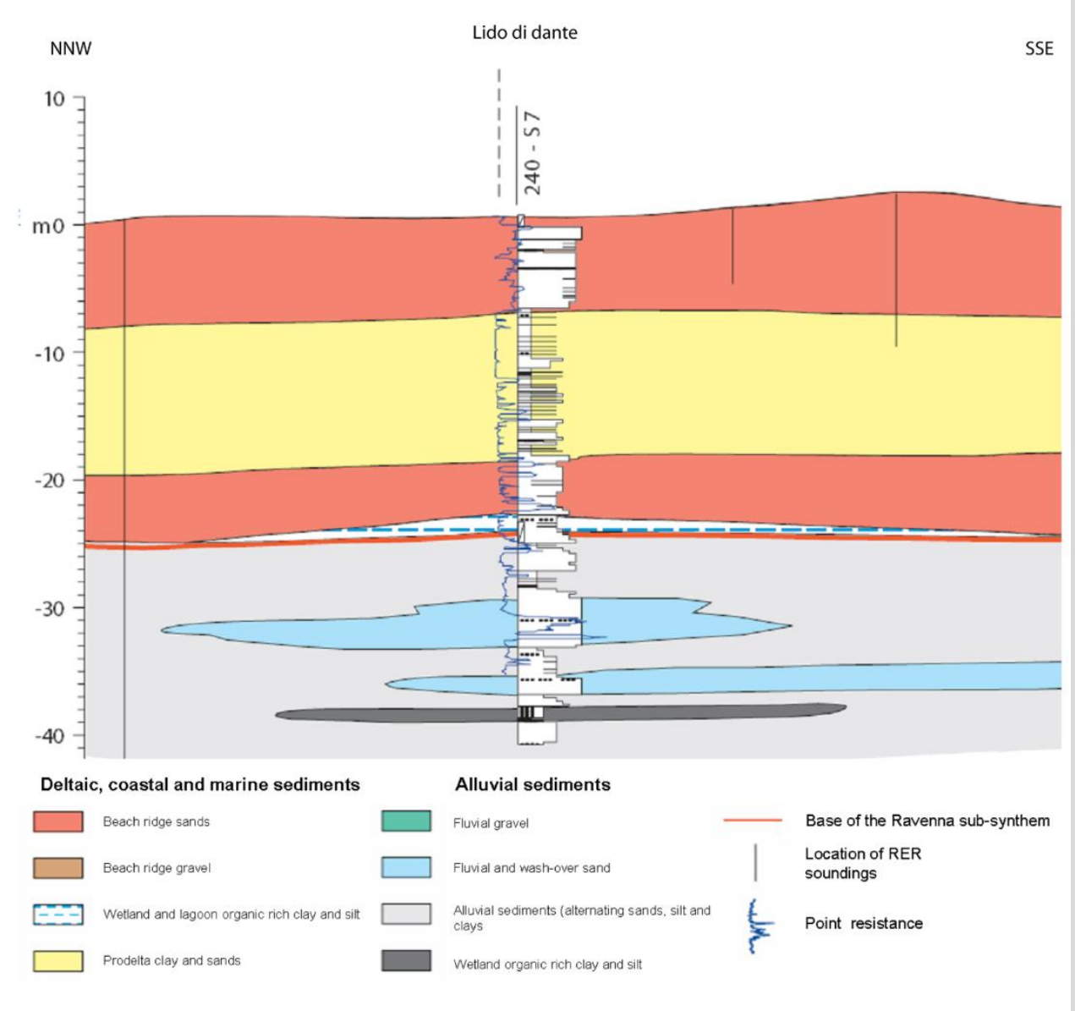
Arsenic concentrations and redox potential distribution in the phreatic aquifer clearly show to be linked. The correlation between arsenic concentrations and redox potential is negative in all monitoring seasons. Within the Arsenic species, As5+ is the most soluble. Therefore, in reducing conditions As concentration should decrease. The negative correlation between As concentration and redox potential suggest that the As mobility is strictly connected to the Iron hydroxides mobility. As concentration in the groundwater shows, in fact, a strong positive relation with Iron concentrations. In situ measurements of Iron speciation indicate that almost all the iron in the sampled water is in the form Fe3+, which belongs to Iron hydroxides. In the phreatic aquifer the arsenic release process is therefore linked to the dissolution of Iron hydroxides, which is caused by redox potential fluctuations. Its mobilisation is favored by the neutrality of the groundwater.

Arsenic source



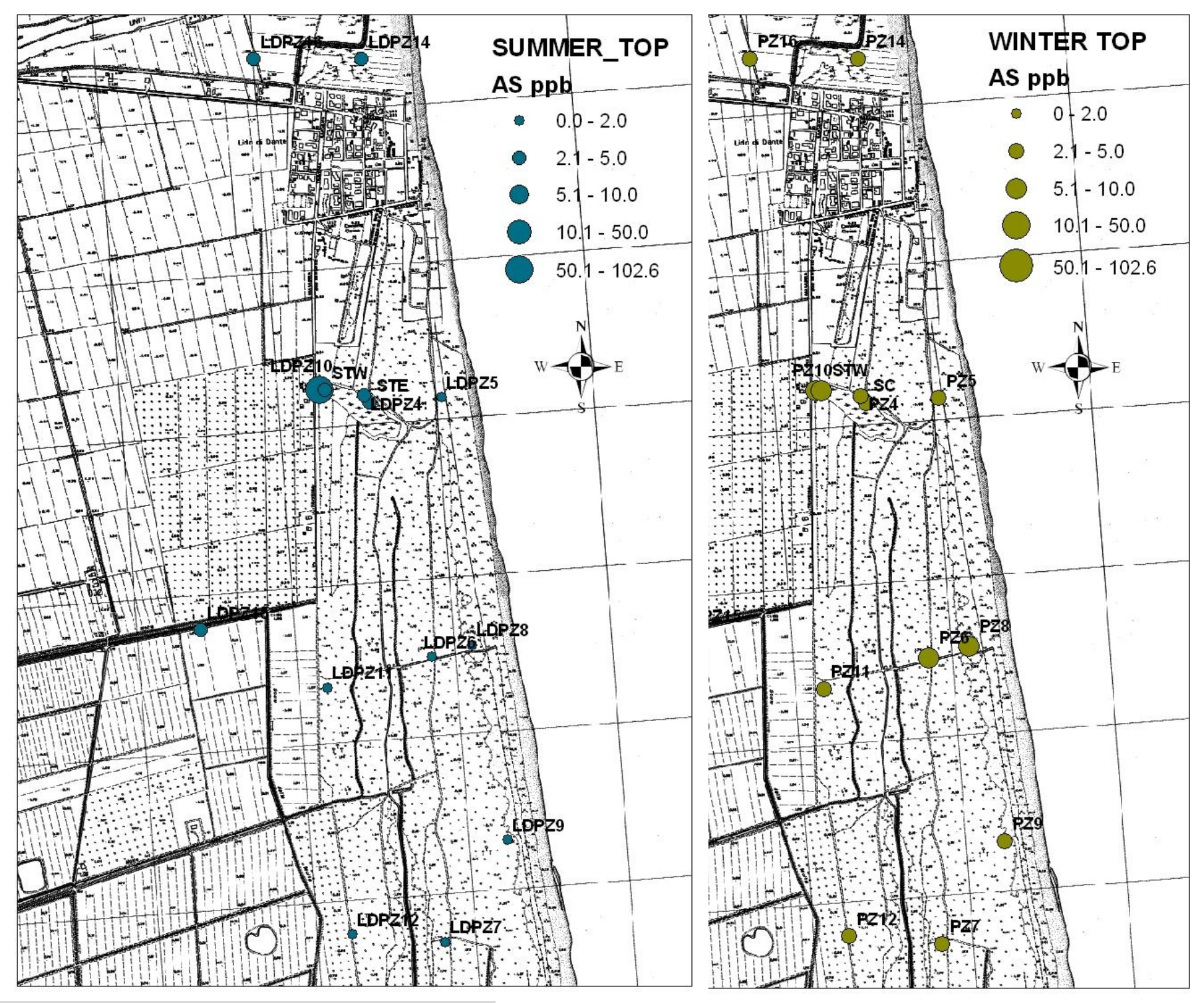
Aquifers of Ravenna province have been classified as belonging to the alluvuial-deltaic group by Regione Emilia-Romagna and ENI-AGIP (1998).
This group consist of a hydrochemical facies characterized by prevailing fine sands and silty sands alternated to organic rich fine sediments with low permeability and reduced water circulation. In this facies the greatest As concentrations (20-50 µg/l) were registered in deep groundwater during 10 years monitoring from 1988-1988 (Farina et al., 2005).
The map is showing the anomaly in Arsenic content (20-50 µg/l) in the deep aquifer in the study area , indicated by the red arrow (modified fro m the official report on water quality, edited by Regione Emilia-Romagna in 2003).

High As concentrations in the deep, confined aquifers are supposed to be linked to Fe hydroxides dissolution, which is caused by redox potential fluctuations (Fuller et al., 1993; Zavatti et al., 1995).
Ravenna deep aquifers (located at the depth of more than 30 m in the study area) are characterized by Fe concentrations ranging from 1000 to 10000 µg/l and Redox potential of ± 50 mV (Farina et al., 2005).
Fe hydroxides such as Goethite (Berner, 1971) are usually associated to fine-grained and organic rich sediments, as clay minerals have a considerable reaction surface and organic matter contains both Fe and As sulphides (Moncure et al., 1992).
According to the Emilia-Romagna region geological survey, these sediments can be found at the depth of more than 25 m in the study area. In the geological section, fine-grained, organic rich sediments are indicated in dark gray, peat discontinuous layers are indicated by the blue dashed lines (modified from Regione Emilia-Romagna webgis).
As far as we know, Arsenic distribution and source in the phreatic aquifer of Ravenna province has not been well investigated yet.
Deep As and Fe enriched groundwater may represent the primary source of Arsenic pollution also in the phreatic aquifer.



Arsenic distribution

The maps show the As distribution at the top of the phreatic aquifer in the study area. At the observation wells located close to the surface water bodies were measured the greatest concentrations (102.6 ppb in the summer and 20 ppb in the winter).



As seasonal distribution in the top aquifer follows the redox potential variations throughout the seasons with negative correlation (see arsenic release section) .
As concentrations in groundwater decrease with depht in the measurements points located in the proximity of surface water bodies. On the contrary, As concentrations slightly increase with depth in the remaining part of the study area.
The highest As concentrations found close to stagnant surface water bodies in both seasons indicates that Arsenic distribution is linked to the processes taking place at the interface between groundwater and surface water, such as evaporation, evapotranspiration of aquatic plants, accumulation of organic matter and the upconing of Fe and As rich groundwater from the bottom of the aquifer.

Soil samples were collected at the observation wells positions and in several additional points. and analysed trhough XRF. The samples collected at the field surface (0-0.05 m) do not contain arsenic. The samples collected at the depth of -0.2 m and of -0.8 m from field surface show an overall enrichment in As content with depth (13 samples on 19). At PZ10 , which is characterized by the greater As content in the groundwater, soil samples were collected at 5 depth from filed surface down to -1.1 m. The diagram show that As is absent until the depth of -0.6 m, which correspond to the upper limit of the water level fluctuation zone. As concentration is maximum at -0.8 m and decrease again below the lower boundary of the water fluctuation zone (-1.1m).
The sediments collected in the hyporeic zone of ponds and ditches located in the pine forest have high Arsenic concentrations (20-38 ppm). Those collected at the dunes slack located at the Uniti river mouth show low Arsenic concentration (0-2 ppm).
The As content of the peat layer located at -25 m from field surface is 16.3 ppm.
The As distribution in the sediments confrim that his direct source are the iron hydroxides of the hyporeic zone and of the vadose zone. Fe and As contained in the Iron hydroxides may originally derive from the deeper groundwater as well as having a local source in the sandy aquifer.