

# **Soil and groundwater contamination by heavy metals in the industrial area of Crotona, Southern Italy**

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## **Abstract**

This work investigates the land contamination by heavy metals of the industrial area of Crotona, a town located on the Ionian coast of Calabria, Southern Italy. A wide collection of soil and groundwater samplings was available either within the area of the industrial installations immediately located on the coast and in the agricultural zone inland, denominated “Area of Dynamical Deposition”. Geo-statistical analysis of soil sampling data and a solute transport numerical model were developed in order to define the land and groundwater contamination level and extension and to investigate the heavy metal contamination sources.

## **Introduction**

Because of the high death-rate for respiratory sicknesses and pulmonary cancer in the Town of Crotona, East of Calabria, Southern Italy, the World Health Organisation (WHO) carried out an epidemiological study whose conclusions encouraged more deepened researches on the hypothesis that an environmental factor could cause the anomalous clinical frame (Frega et al. [1]).

This study, on the basis of a wide collection of soil and groundwater samples, investigates the land and water contamination level of the coast of Crotona (Troisi et al. [2]). The study area delimited by Passovecchio River, at North, and by Esaro River, at South, is considered, including the industrial area of the Pertusola plant and the inland agricultural area located immediately behind the industrial installations.

In particular the soil and groundwater contamination by cadmium was studied. The use of geo-statistical method of spatial analysis such as indicator kriging allowed the assessment of soil contamination sources.

The implementation of a solute transport model allowed to evaluate the current state of groundwater contamination (Gambolati et al. [3]).

## The study-area

The study area is located at North-East of the centre of Crotona, two kilometres distant. It includes an industrial district, located on the Ionian coast, and an inland wide agricultural area, whose subsoil is suspected to hide one of the largest archaeological deposits of the Hellenic age, when the city of Crotona was an important crossroad of the Great Greek civilization (Figure 1).

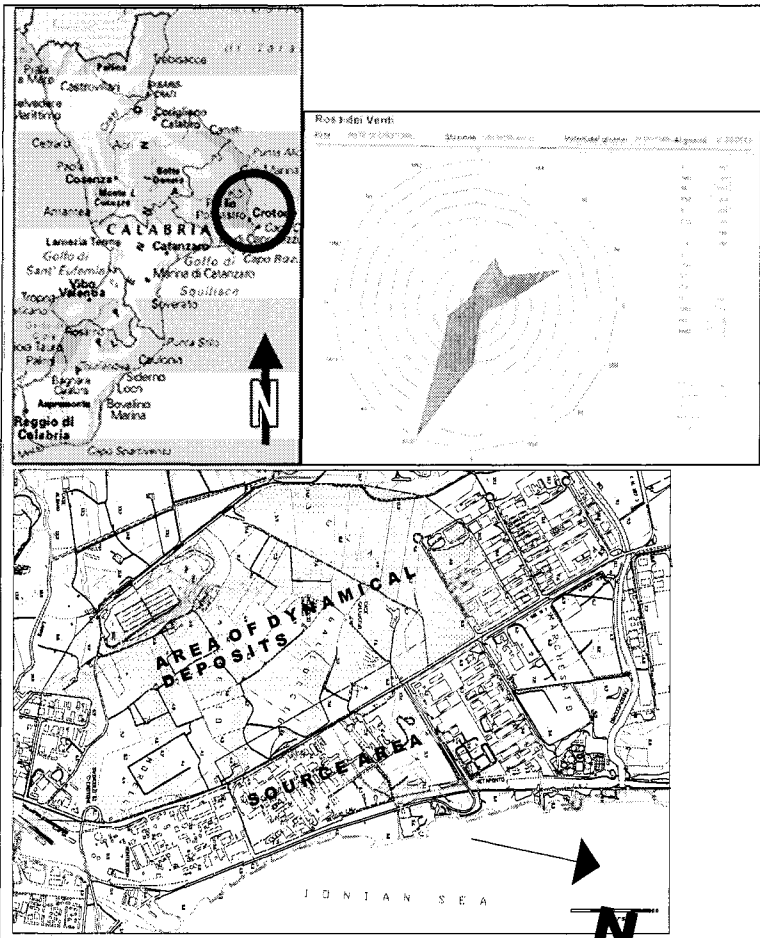


Figure 1: Geographical location of the study-area and its anemometric regimen

The industrial district includes the Pertusola plant for zinc, cadmium, copper, lead sulfate and silver. The plant is currently almost quite inactive.

The agricultural area is delimited by the Esaro River at South and by the Passovecchio River at North. Its orography is prevalently tabular and lightly hilly. Hereinafter the site of the Pertusola plant and the agricultural land situated behind the industrial installations will be indicated respectively as "Source-Area" (SA) and "Area of Dynamical Deposition" (ADD) (Figure 1). Because of the workings carried on in the Pertusola plant and of the predominance in the area of winds originated by North-East (Figure 1), in fact, there are enough elements to do the hypothesis that the contamination by heavy metals pointed out within the Pertusola area has also impacted the agricultural area, according to Figure 2 and Table 1.

### **Geological setting and groundwater flow characterization**

In the SA 90 drilling bores, with different depths, were executed and many of them were completed to realize wells and a network of 21 piezometric observation points (Figures 3, 4). Two pumping tests were carried out in order to estimate the subsurface hydraulic properties. In the ADD a pumping test was also carried out, using existing wells and a number of geoelectrical surveys were executed. The above said hydro-geological and geophysical tests showed that: 1) from a geological point of view the subsoil of the study-area includes a basic formation consisting of clay and loam rock and an upper formation consisting of sand, sandstone; 2) the alluvial deposits, produced by the erosion of the surrounding hills, consist of lightly silty sands, mixed to gravel elements, and show very high hydraulic conductivity ( $10^{-3}$  m/s); 3) groundwater system consists of a phreatic aquifer characterized by a mean thickness  $H = 12$  (m), with a very superficial water table (5 – 6 (m) from ground surface) and an hydraulic mean transmissivity  $T = 0.013$  m<sup>2</sup>/s.

Using this hydro-geological information, a flow model was implemented in order to study the groundwater flow in the study-area. Figure 5 represents the flow model results in the whole study-area. Figure 6 reports groundwater flow model issues, zoomed on the Source-Area.

### **Soil and groundwater contamination**

In Figure 7 the soil sampling network is represented. As shown, soil samplings were collected either in the SA and in the ADD. Groundwater sampling network, on the contrary, as shown in Figure 8, concerned with SA only.

Table 2 shows the soil highest concentrations of heavy metals such as As, Cd, Cu, Hg, Pb, Zn, compared with the threshold value of the Italian land contamination regulation. Table 3 shows the highest concentration of heavy metals in groundwater samplings.

Soil samplings analysis allowed to assess that soil contamination by heavy metals such as As, Cd, Cu and Zn, concerned with both SA and ADD areas

while contamination by Pb and Hg appeared to be confined within Pertusola plant area.

Groundwater samplings analysis showed a strong contamination by heavy metals such as Cd and Zn, while As, Cu, Hg, and Pb showed acceptable or not high concentrations.

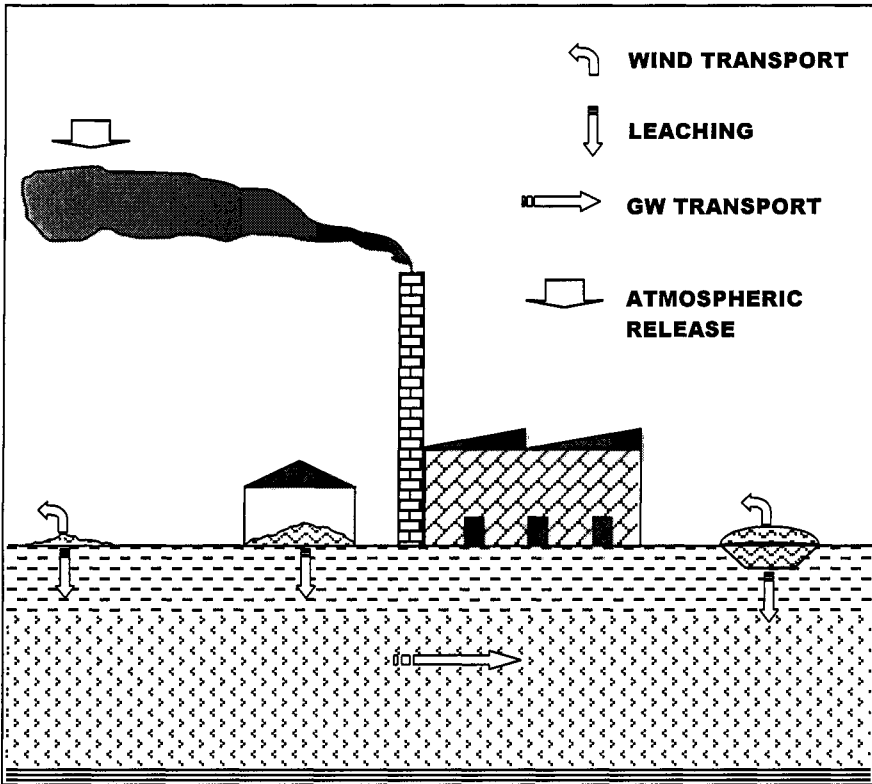


Figure 2: Contamination source phenomenological scheme

Table 1: Pertusola contaminants and contaminant sources

CONTAMINANT	PROBABLE SOURCE
As	Blend store, furnace tailings, zinc ferrites
Cd	Lixiviation products and Cd recovery process
Cu	Lixiviation products and zinc ferrites
Hg	Blend store and zinc ferrites
Pb	Zinc ferrites
Zn	Zinc working and zinc ferrites

Table 2: Soil sampling highest concentrations of heavy metals

METAL	SOURCE- AREA (mg/Kg)	AREA OF DYNAMICAL DEPOSIT (mg/Kg)	ITALIAN THRESHOLD VALUE (mg(Kg)
As	2682	3310	50
Cd	2173	993	15
Cu	4455	1570	600
Hg	197	0.5	5
Pb	37700	615	1000
Zn	80020	4367	1500

Table 3: Groundwater sampling highest concentrations of heavy metals

METAL	SOURCE- AREA ( $\mu$ g/Kg)	AREA OF DYNAMICAL DEPOSIT ( $\mu$ g/Kg)	ITALIAN THRESHOLD VALUE ( $\mu$ g(Kg)
As	55	2.7	10
Cd	20300	0.3	5
Cu	150	0.1	1000
Hg	1	0.5	1
Pb	490	0.1	10
Zn	7875000	52	3000

In order to investigate about soil contamination origin a geostatistical analysis was carried out on the Cd concentration data. The indicator kriging approach was used, fixing the following cut-off values: 15 (mg/Kg), i.e. the threshold value in the Italian law, 75 (mg/Kg), i.e. 5-times the Italian threshold value, and 150, i.e. 10-times the Italian threshold value. Directional variograms were, thus, built for the defined indicator variables Cd(15), Cd(75), Cd(150) in order to investigate the presence of preferred directional characters in the spatial distribution of the Cd concentration data. Range and sill of each variogram were plotted in the radar diagrams represented in Figure 9, which showed as the sill of the North-East variograms always prevails on the sill of the other directional variograms. This result confirms the phenomenological scheme hypothesized in Figure 2, according to which the soil contamination in the Pertusola plant area impacted also the inland agricultural area, thanks primarily to the predominant winds from North-East. The sill, in fact, is the geostatistical parameter associated with the spatial variability and dispersion of a land attribute.

In order to assess the possible evolution of the groundwater contamination by Cd, a mass transport model was implemented. Figure 10 shows the current scenery of groundwater contamination, as it was given by the numerical model used. It results that a contaminant plume has already reached the Ionian sea of Crotona; therefore, a land remediation action has to be finalized primarily to the stop of it.

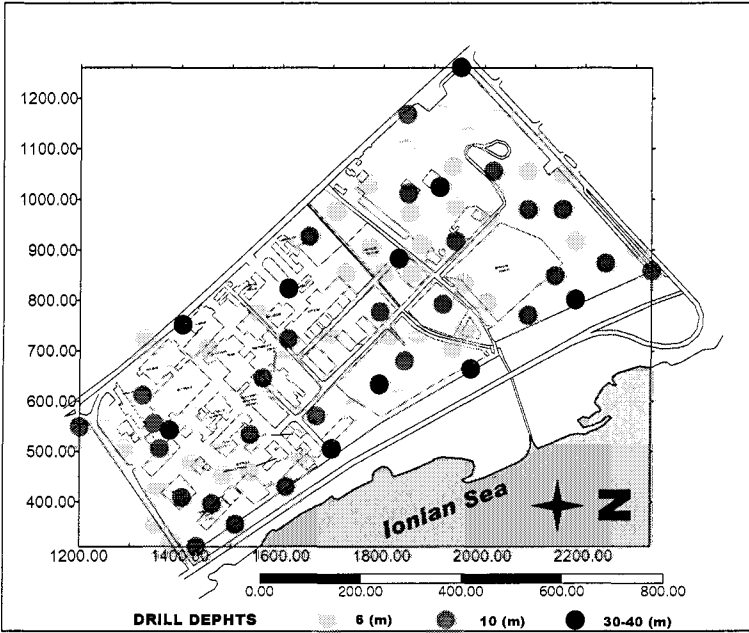


Figure 3: Location of the drilling-bores executed in the Source-Area

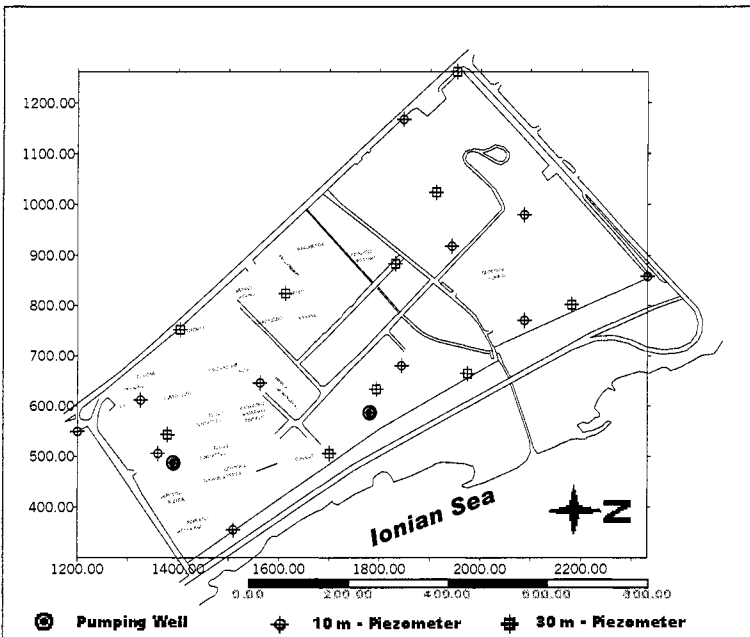


Figure 4: Location of the wells and piezometric observation points

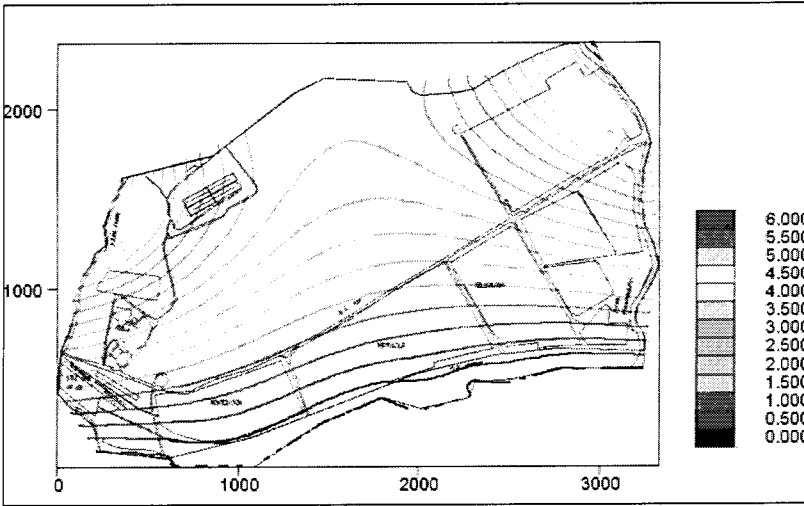


Figure 5: Output of the flow numerical model in the whole Study-Area

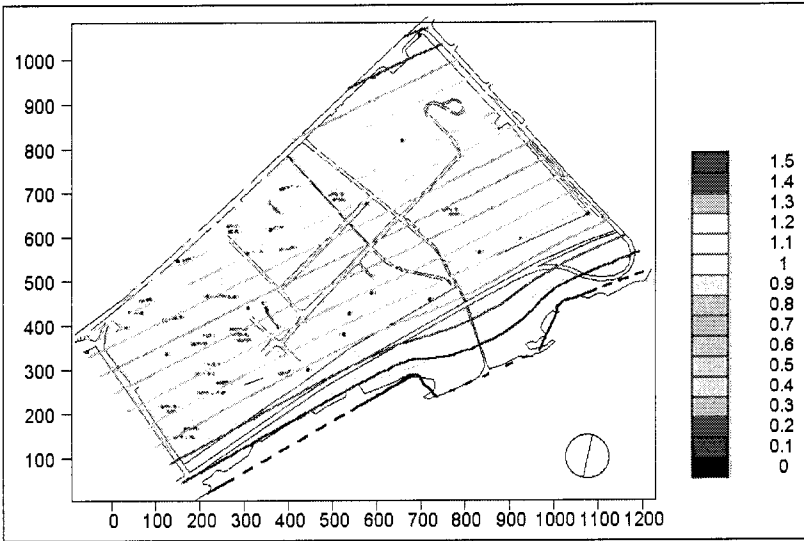


Figure 6: Output of the flow numerical model in the Source-Area

## Conclusions

Land contamination by heavy metals of the industrial area of Crotona was investigated, using a wide collection of soil and groundwater samplings.

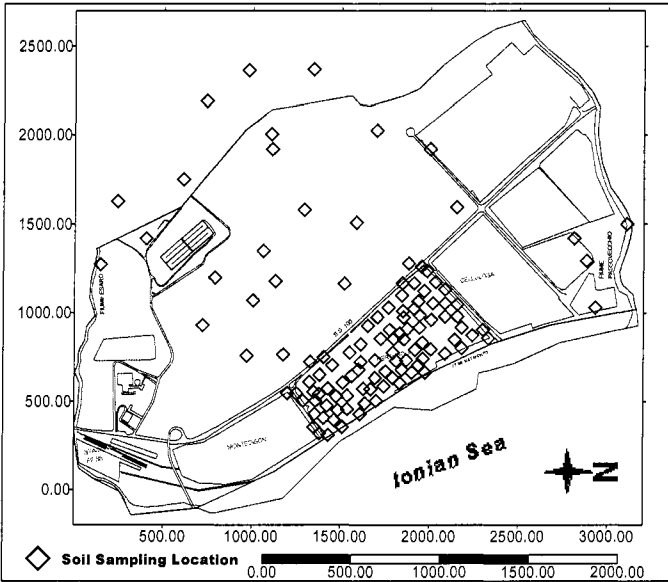


Figure 7: Location of the soil sampling points in the Study-Area

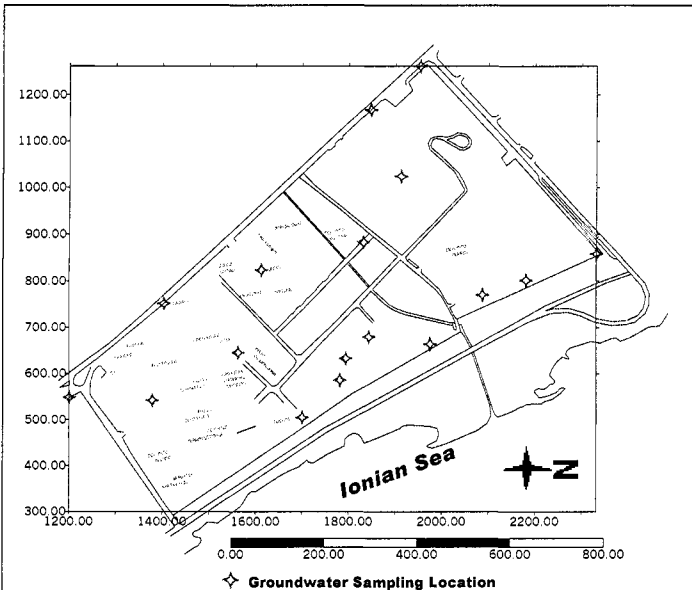


Figure 8: Location of the groundwater sampling points in the Source-Area



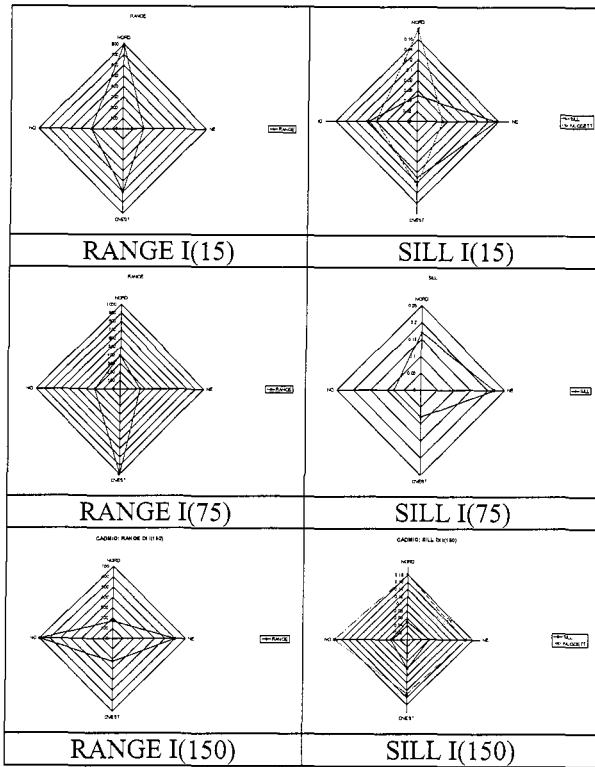


Figure 9: Radar diagrams for the detection of the contaminating sources

Geo-statistical analysis of soil sampling data and a solute transport numerical model were developed in order to define the land and groundwater contamination level and extension and to investigate the heavy metal contamination sources. Contamination by heavy metals impacts either the soil or the subsoil and groundwater systems, with high concentrations of arsenic, cadmium, copper, lead, mercury and zinc. The industrial installations on the coast, demanded to the production of Cu, Zn and Cd were detected as the main sources of the contamination. A subsurface contaminated plume has already reached the Ionian sea and a land remediation action has to be finalized to the stop of it.

In land and groundwater remediation actions the engineering design uncertainty level is greater than in most traditional engineering practice, because a good knowledge of the subsurface systems is required and we have great uncertainty not only about the system parameter and properties but also about the very geometry of the system we are trying to analyse.

Decision-makers base their decisions on an economic analysis of the alternatives. This analysis takes into account the costs and benefits of each alternative, but it must also give weight to the associated risks of failing to meet

design objectives. Risk reflects uncertainty in the technical analysis and in the groundwater flow and transport modelling: in many hydrogeological settings, the risks associated with decision-making are high. Therefore scientific research must be driven towards the investigation of viable methodologies and tools, resting on a risk-based philosophy, which are able to link the economic framework in which decisions are made and the results of the technical and modelling analysis on which decisions are based.

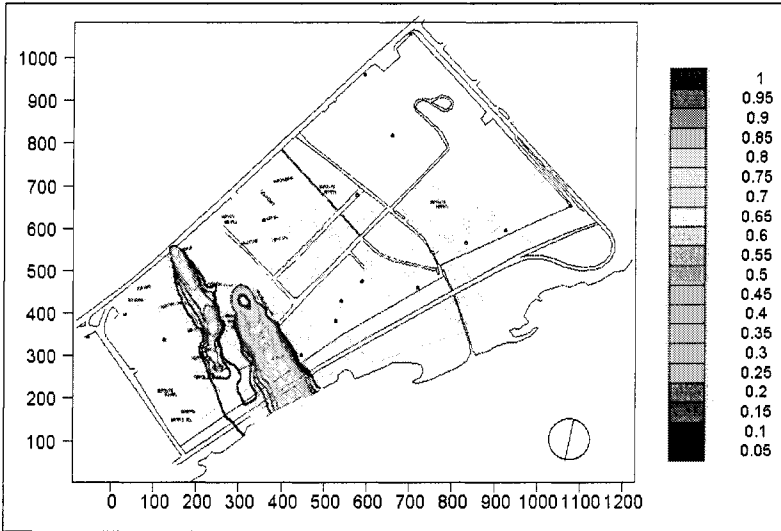


Figure 10: Output of the cadmium solute transport model

## References

- [1] Frega G., Troisi S., Straface S., Chidichimo G., Liguori A., Nicoletta M., Critelli M., Angelillo I., Nobile C., Pavia M., Costa I. – Epidemiological study on the respiratory pathologies and pulmonary cancer in Crotona city, South of Italy, *International Journal of Medicine, Biology and the Environment*, v. 28 n. 2, pp 123 – 133, 2000
- [2] Troisi S., Straface S., Migliari E., Gagliardi V. – First approach to the remediation of the industrial area of Crotona, South of Italy, in *Proceedings of the International Workshop on Contaminated Sites Assessment and Remediation: The New Perspectives*, pp 152 – 159, Milan 2000.
- [3] Gambolati G., Paniconi C., Putti M., - Numerical modeling of contaminant transport in groundwater, in *Proceedings of the International Conference on Migration and Fate of Pollutants in Soils and Subsoils*, pp 381 – 410, Acquafredda di Maratea 1992