# Methodological Approach for Ground Contamination Assessment and Remediation of Brownfields

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*Abstract*: A methodology is presented for ground contamination assessment and remediation of brownfields, emphasizing the application of geostatistical models in sequential stages of site investigation. The methodology is applied to a former industrial area in Barreiro (Portugal), in the left margin of Tagus River, 7km south of Lisbon. The area, where heavy industry (chemical, metallurgical, etc.) operated during the last century, is presently submitted to environmental requalification planning for urban redevelopment.

*Key-words:* ground contamination, site assessment, remediation, geostatistics, brownfields, heavy metals

## 1 Introduction

Soil is a high value natural resource, hardly renewable at human scale, whose chemical contamination leads to its economical loss.

The growing need to promote the redevelopment of *brownfields* instead of the systematic use of *greenfields*, calls for the standardization of contaminated site assessment procedures.

A methodology for ground contamination assessment and remediation of brownfields, integrating the application of geostatistical models in different stages of site investigation is presented.

## 2 Methodology

The methodology integrates the application of geostatistical mathematical models as key tools for the reduction of site investigation costs associated to land contamination evaluation and site remediation plan. It encloses three site investigation phases:

<u>1st phase – Preliminary investigation phase</u>

This phase aims at identifying evidences of contamination, mainly using screening methods. It comprises:

- collection of relevant historical data, such as, site activity and industrial processing, existing field survey data, technical reports, maps, etc., evaluation of ground characteristics, namely, geological and hydrogeological maps and topography;
- Spatial identification of "hot spots" using low cost data screening methods (as photo ionizer detectors (PID), X-ray fluorescence spectrometers (XRF)), including geophysical survey (electromagnetic, georadar and resistivity surveys).

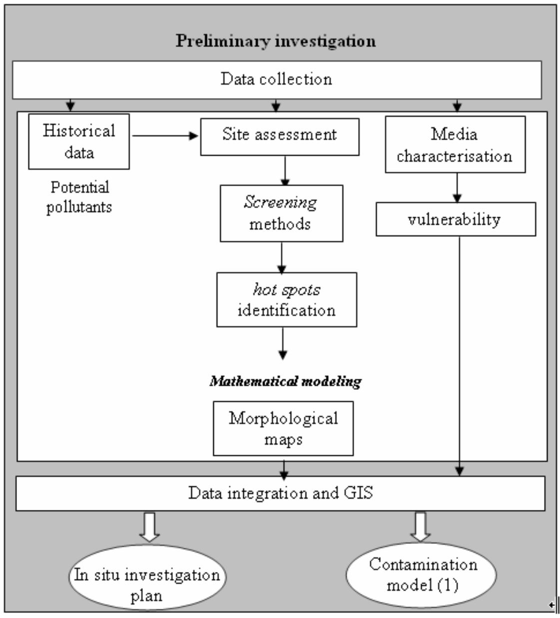

Fig.1 – Main steps for preliminary investigation phase (in [2])

Geostatistical modelling, together with GIS, is used to produce surface pollution maps and to define the geometry of soil sampling campaign and identification of operational site constraints. Figure 1 illustrates main steps used for preliminary investigation phase.

2nd phase – Exploratory investigation phase

This phase aims at the evaluation of ground contamination (soil and groundwater) and the definition of the contamination model.

- Site investigation for soil and groundwater, including sampling,
- identification of chemical contaminants,
- Identification of physical media characteristics (such as soil type, permeability, pH, groundwater electrical conductivity, etc.),
- Characterization of terrain morphology.

Geostatistical modelling is used for the identification of contamination plumes. Estimated maps resulting from this phase define the type and extension of contaminated areas, quantification of contaminated media and uncertainty areas.

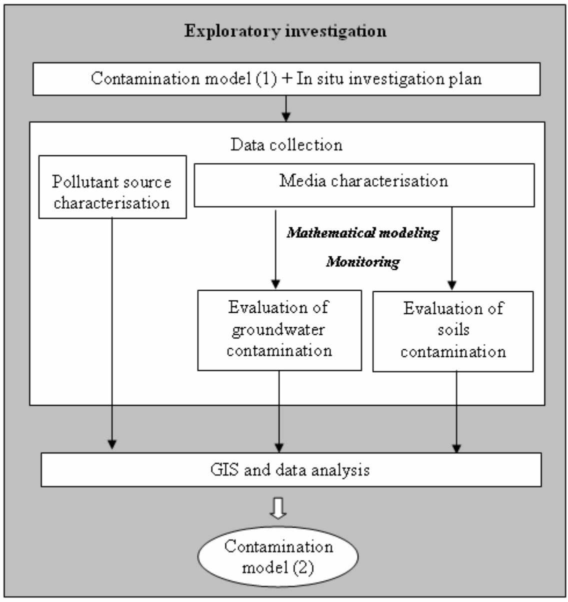

Fig.2 – Main steps for exploratory investigation phase (in [2])

If necessary, a second sampling campaign is planned in order to clarify uncertainty areas.

3rd phase – Detailed investigation phase

During this phase a $2^{nd}$ field sampling campaign is performed to refine contaminated areas boundaries. Indicator kriging geostatistical modelling is used to calculate volume of contaminated soils for distinct scenarios, depending on required reference values.

Generally, surface soil and groundwater remediation criteria are based on “Guidelines for use at contaminated sites in Ontario” [1].

Geostatistical modelling is also used to quantify contaminated media and create scenarios for the remediation plan, based on estimated risk maps and uncertainty areas.

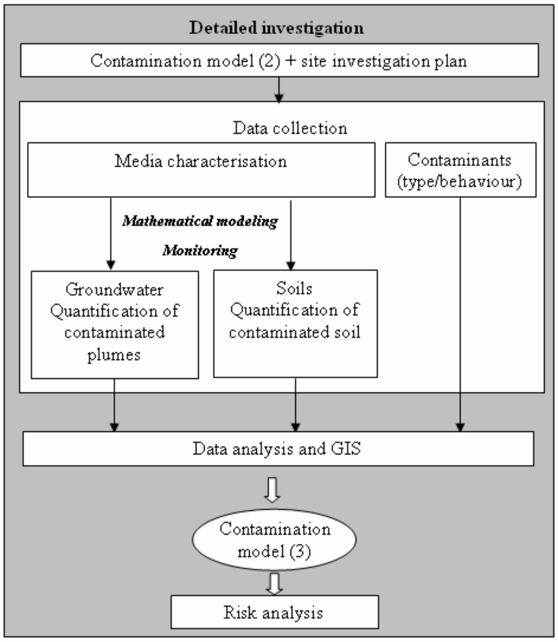

Fig.3– Main steps for detailed investigation phase (in [2])

## 2 Barreiro Case Study

The methodology was applied to a former industrial area in Barreiro (Portugal), located in Tagus river estuary, 7km south of Lisbon [2, 3], presently under the process of environmental requalification for urban redevelopment (Fig. 4).

The priority area, of about 30 hectares was, during the last century, scenario for heavy industries, mainly chemical for the production of sulphuric acid, phosphate acid, copper and sodium sulphates, copper, lead, gold and silver metallurgies and others, resulting in a widespread of industrial waste containing heavy metals delivered to soil and groundwater.

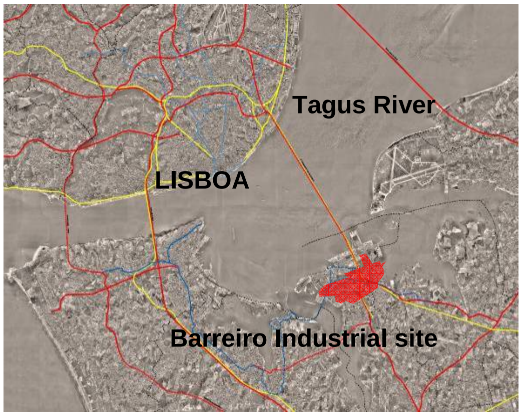

Fig. 4 – Location of Barreiro Industrial site

## 2.1 Site assessment

During the preliminary investigation phase a set of screening methods were performed:

- XRF *Niton* analyzer survey, for heavy metals screening (83 measurements and 4 soil sampling for calibration);
- PID *Photovac* 2020, for VOC analysis in soils and infrastructures;
- Electrical resistivity survey (12 profiles up to 13.5m depth), for identifying ground anomalous concentrations in dissolved salts and metals
- Electromagnetic conductivity survey with *Geonix* EM31 method (19 profiles) for identifying anomalous concentrations in dissolved salts and metals, in saturated terrain (3 and 6 m depth)
- Georadar survey with *Ramac GPR* equipment, for detection of buried infrastructures.

The XRF screening campaign allowed the identification of several chemical elements at the surface, mainly in the south area of the site which could be related to the location of the old metallurgical plants (Fig.5).

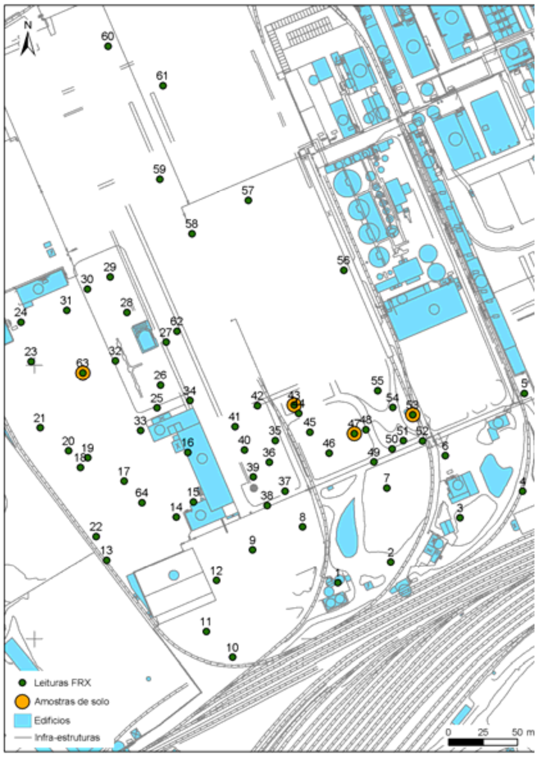

Fig.5 – Location of XRF measurements (in [2])

Hotspot contaminated areas were obtained by the estimation of XRF chemical values using geostatistical tools (Fig. 6).

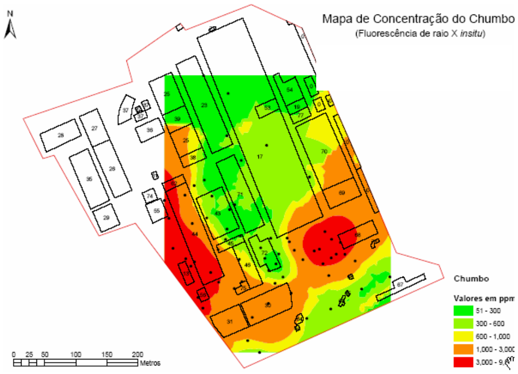

Fig.6 – Example of Pb estimated map (XRF measurements (in [2]))

Geophysical surveying was preceded by removal of vegetation and superficial ground cleaning.

For the electrical resistivity survey it was defined a set of 12 resistivity profiles (RE), with the following geometry (Fig. 7): 10 longitudinal profiles, with an extension of 235m in average, spaced about 50m. In each profile there were placed 48 electrodes. Two other profiles where made, with about 50m length and 24 electrodes, in order to refine underground electrical properties. The first geometry allowed an investigation depth around 13.5m and the second one about 6m.

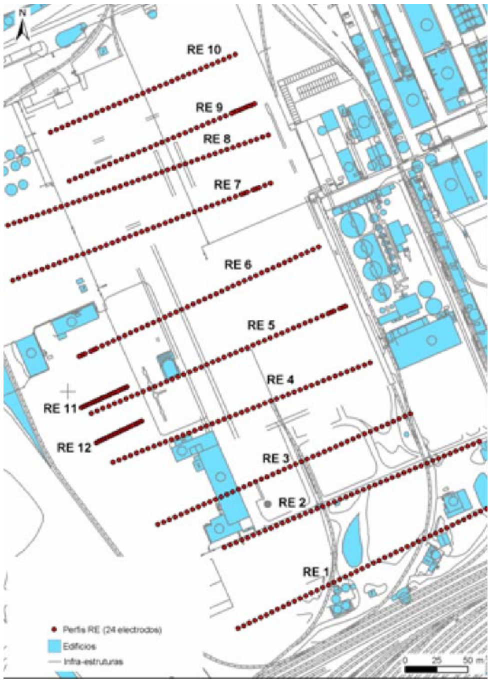

Fig.7 – Resistivity profiles geometry (in [2])

Figure 8 shows some of the output resistivity profiles, converted in electrical conductivity values, in order to compare with electromagnetic mapping.

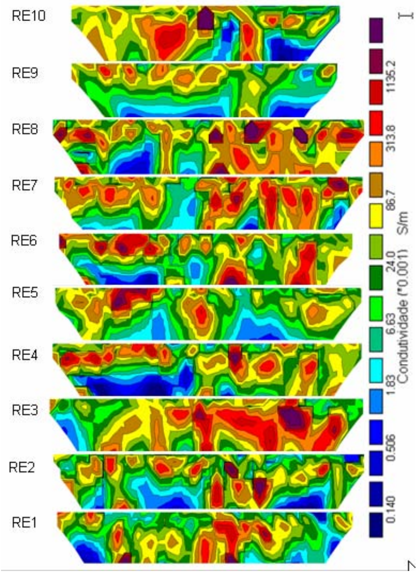

Fig.8 – Illustration of a resistivity profiles (values in electrical conductivity (x10$^{-3}$ S/m)) (in [2])

Electrical conductivity values showed great contrast: the high conductivity values could be related with infrastructures (electrical cables) and dissolved salts or metallic elements concentrated in the soil and the lower conductivity values may be related to landfill materials, foundations and concrete basements.

For assessing the physical properties of the saturated levels there were implemented a set of 19 electromagnetic profiles, spaced about 25m, with an extension of 500m average in length, as illustrated in figure 9.

Fig.9 – Geometry of electromagnetic campaign (in [2])

The readings were taken from 10 to 10m over the profiles. Figure 10 shows, as example, electromagnetic field measurements.

Fig.10 –Electromagnetic field readings (in [2])

Figure 11 illustrates the electromagnetic conductivity maps obtained for 3m and 6m depth levels.

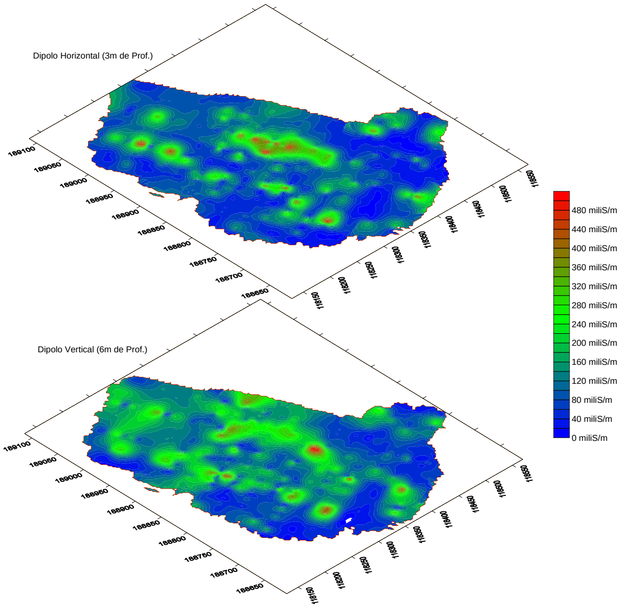

Fig.11 – Electromagnetic conductivity maps; 3m and 6m depth, respectively (in [2])

Due to several surface and underground structures (landfill of construction materials, infrastructures, groundwater…) electromagnetic conductivity pattern is very heterogeneous and values increase at 6 m depth. As observed in figure 11, apparently there is a

displacement of the highest values of conductivity from SSW to NNE which means that groundwater flow direction seems to be from SSW to NNE.
For the detection of buried infrastructures a georadar survey was carried out which allowed the identification of several unmapped infrastructures, as shown in figure 12.

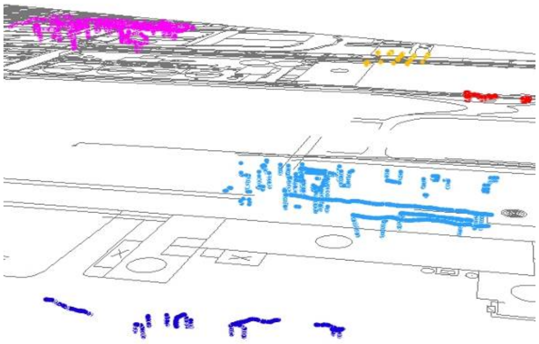

Fig.12 – Identification of buried infrastructures through georadar survey (in [2])

Based on preliminary data, a conceptual contamination model was designed, taking into account the following elements (Fig. 13):
- the <u>source</u> – industrial waste spread all over the area;
- the <u>path</u> – soil and groundwater as primary targets, and, simultaneously, as main contamination pathways,
- the <u>target</u> – humans and biota through soil and groundwater media.

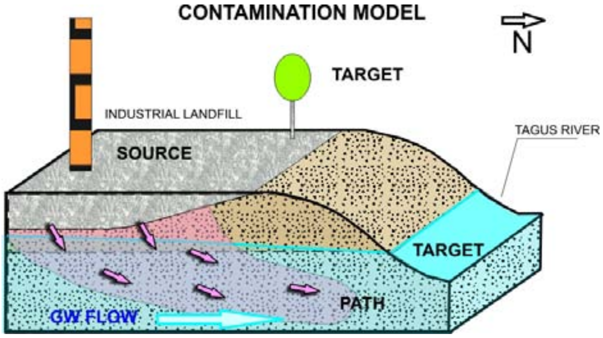

Fig.13 – Conceptual contamination model (in [2])

Preliminary investigation data was the basis for the definition of a field survey, including trial pits and drilling campaign for soil and groundwater assessment (Fig. 14 and Fig. 15).

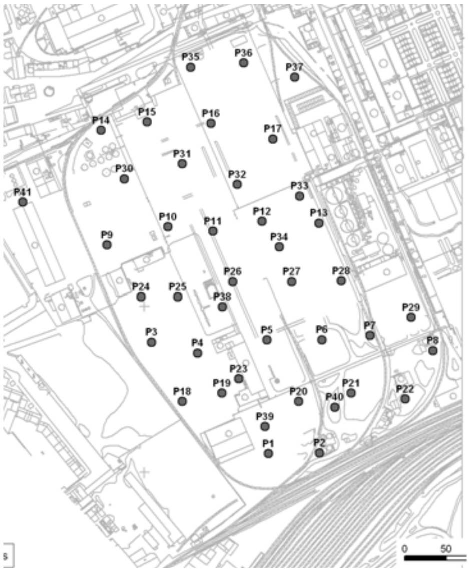

Fig.14 – Field survey: trial pits campaign for soils (in [2])

Fig.15 – Field survey :drilling campaign for groundwater (in [2])

<u>Exploratory investigation phase</u>
The exploratory investigation phase aims at the confirmation of contamination hypothesis, determination of the nature and concentration of contaminants as well as the definition of contamination patterns, in soils and groundwater. In this phase geostatistical modelling is used.
Exploratory investigation phase comprised the following field work:

- 41 trial pits (maximum 4m depth) and collection of 62 soil samples at 3 levels;

- 8 drilling boreholes (maximum 10 m depth) for soil and groundwater sampling.

Collected samples where submitted to basic geotechnical and chemical laboratory tests. Interpretation of borehole logs enabled the execution of lithological profiles (Fig. 16 and Fig. 17).

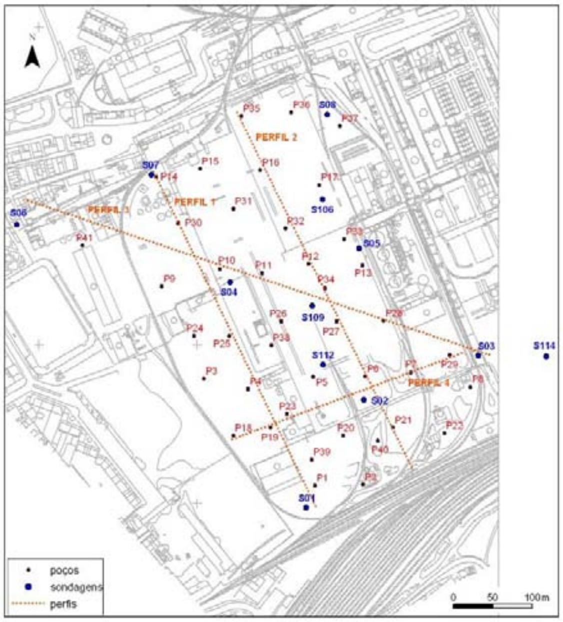

Fig.16 – Exploratory site investigation plan: trial pits (P), boreholes (S) lithological profiles location (in [2]).

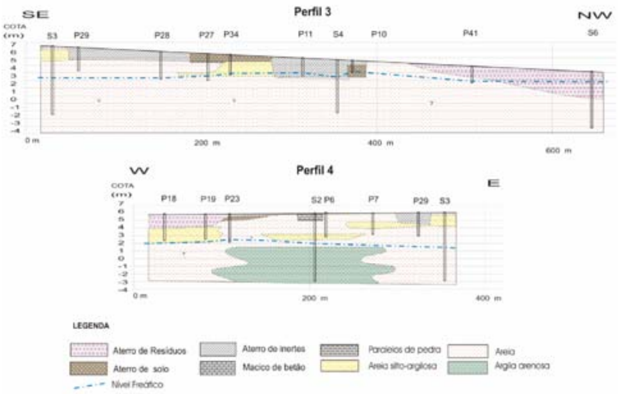

Fig.17 – Example of the lithological profiles (in [2]).

From the 260 organic and inorganic chemical elements analyzed with TerrAttest® method, only five elements presented chemical concentrations above reference values [1]: As, Ba, Cu, Pb and Sb as illustrated in figures 18 to 22, for the superficial level (between 1m and 2.5m depth).

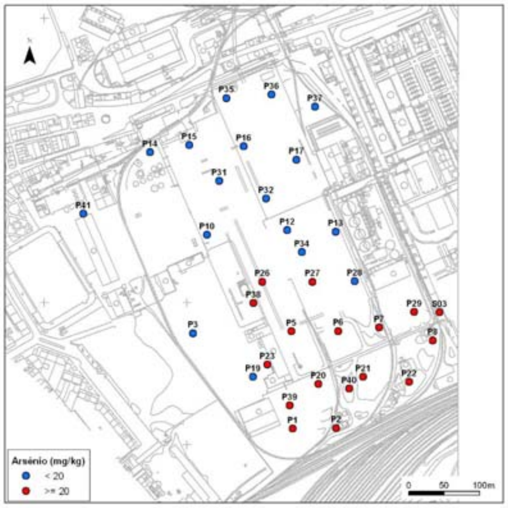

Fig.18– Spatial distribution of As >=20mg/kg (in [2])

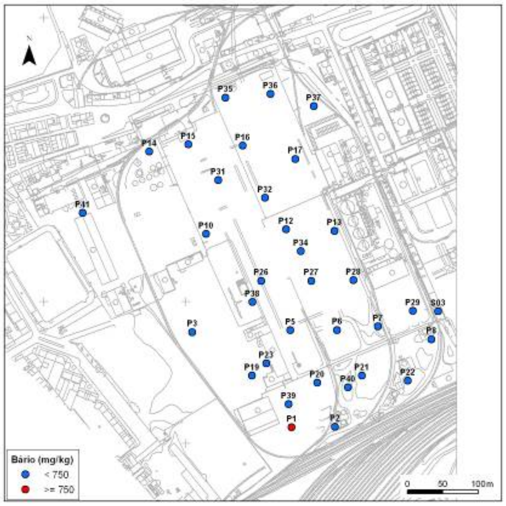

Fig.19– Spatial distribution of Ba >=750mg/kg (in [2])

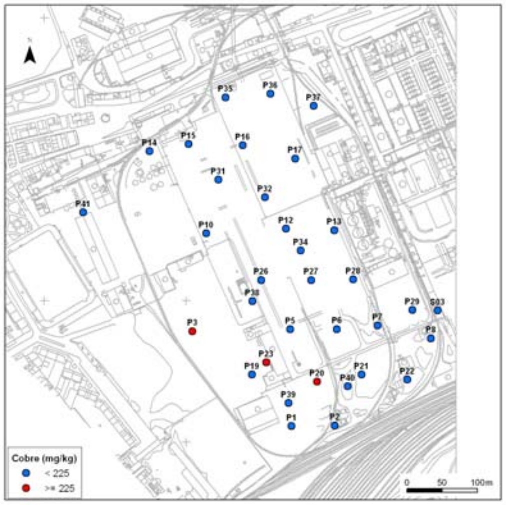

Fig.20– Spatial distribution of Cu >=255mg/kg (in [2])

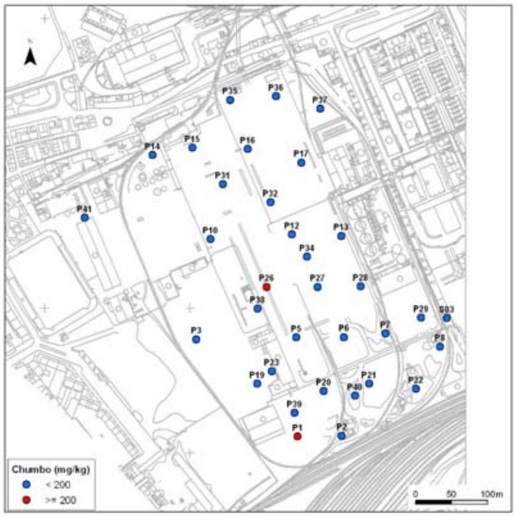

Fig.21– Spatial distribution of Pb >=200mg/kg (in [2])

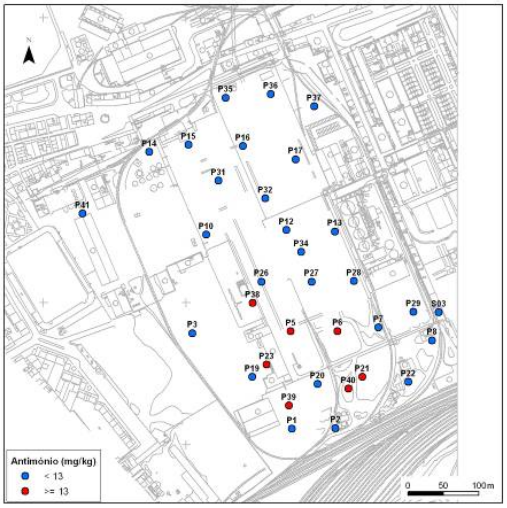

Fig.22– Spatial distribution of Sb >=13mg/kg (in [2])

As it could be observed from the figures, only arsenic (As) occurrences are significant, with the higher concentration values located at the southern part of the industrial area. Figure 23 shows the statistical distribution of arsenic grades in soils.

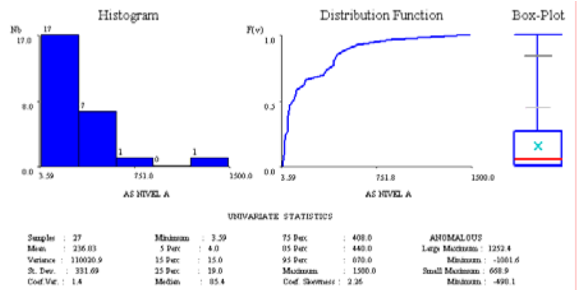

Fig.23– Statistical distribution of As grades in soil (in [2])

Detailed investigation phase aimed at the refinement of the boundaries of contaminated areas. The following works were performed:

- 11 additional trail pits, with the collection of 23 soil samples (Fig. 24)

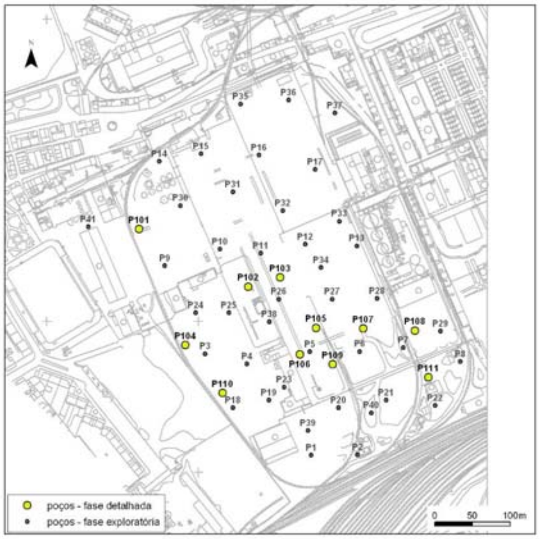

Fig.24 – Detailed phase: trial pits campaign for soils (in [2])

- 14 boreholes, up to 14m depth, for soil and groundwater sampling (Fig. 25)

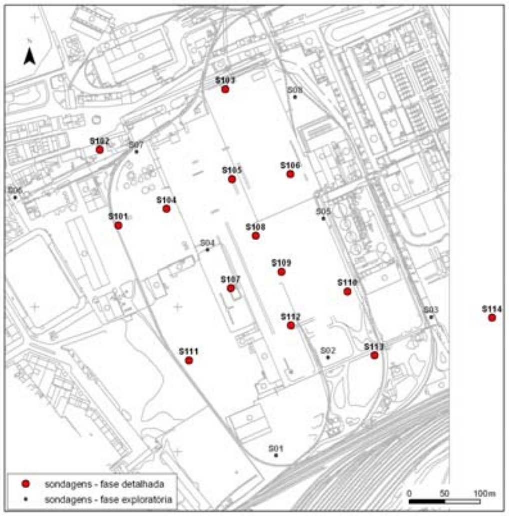

Fig.25 – Detailed phase: drilling campaign for soils (in [2])

For the whole study area there were collected and analyzed a total of 101 samples of soil, for three different levels of depth, corresponding to a total of 59 sample locations (8 wells and 41 trial pits, at the stage of exploratory research and 14 wells and 11 trial pits at the stage of detailed investigation phase).
In this phase geostatistical modelling is used for

estimating contaminated plumes, in soils and ground water [4; 5; 6]. Mathematical flow modelling was performed for the characterization of aquifer dynamics [7].

The main deliverables of the detailed investigation phase are: (i) the final contamination model of the site; (ii) mapping of contaminated areas and quantification of contaminated and non-contaminated media; (iii) identification of groundwater flow (speed and direction); (iv) identification of groundwater contaminated plumes and prediction of contamination pathways and; (v) the definition of the site human health conceptual risk model (Fig. 26) for the prediction of human health risk scenarios [8].

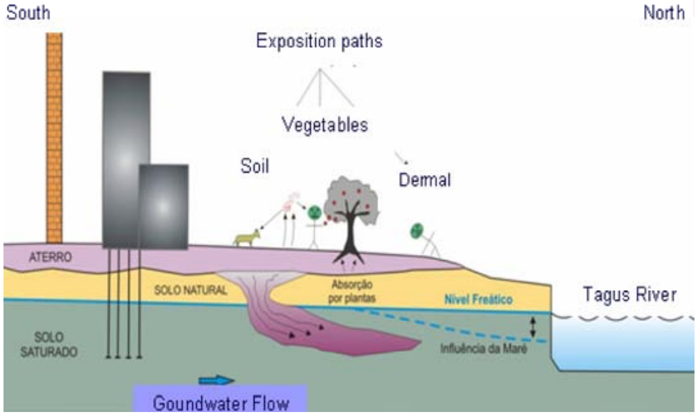

Fig.26 – Conceptual human health risk model and scenarios (in [2])

## 2.2 Site modelling

During each site investigation phase, geostatistical models, using indicator kriging methods [5; 9] and software *geoMS* [5], were applied in order to estimate the morphology of contaminated areas.

Indicator kriging method estimates the probability of a local to present chemical elements content above a certain reference value [5; 9].

Indicator variables (*I(x)*) are obtained as (equation 1):

$$I(x_i) = \begin{cases} 1 \ \ if \ \ x_i \in X \\ \qquad\qquad\qquad and \ \ i = 1, \dots, N \\ 0 \ \ if \ \ x_i \in X^c \end{cases} \qquad \text{(Equation 1)}$$

$I(x_i)$ – indicator variable at point $x_i$;
$i, \dots N$ - number of samples
$X$ – contaminated area

The spatial contiguity of $X$ and $X^C$ can be measured by indicator variogram $\gamma_I(h)$, defined as (equation 2):

$$\gamma_I(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} \left[ I(x_i) - I(x_i + h) \right]^2 \qquad \text{(Equation 2)}$$

$h$ – distance between samples
$N(h)$ – number of data pairs within the class of distance $h$
$i$ – sample location; 1…. $N$
$x_i$ – value of sample at location $i$
$\gamma_I$ $(h)$ – indicator variogram value for lag distance $h$

Indicator variogram is a measure of how often two $z$ values, separated by a vector $h$, are on opposite sides of a threshold value [10].

Thus, for each point $x_0$ of a regular grid $A$, the probability of $x_0$ belong to $X$ (above threshold value) can be estimated as a linear combination of the neighbouring samples of $x_0$ $I_z(x_\alpha)$, $\alpha$ = 1 to $N$, as (equation 3):

$$\left[ I_z(x_0) \right]^* = \sum_{\alpha=1}^{N} \lambda_\alpha(z) I_z(x_\alpha) \qquad \text{(Equation 3)}$$

$x_0$ - location of the point to estimate;
$\lambda_\alpha$ - weight of each sample $\alpha = 1, \dots, N$.
$I_z(x_\alpha)$ – probability of $x_0$ belong to $X$

For each sample, chemical elements where transformed into indicator variables (equation 1), based on predefined reference values [1]. From the five chemical elements detected, only arsenic (As) presented spatial significance for geostatistical estimation. The structure of arsenic plume on top soil level could be analyzed by the variogram presented on figure 27, for the top level of the soil (equation 2).

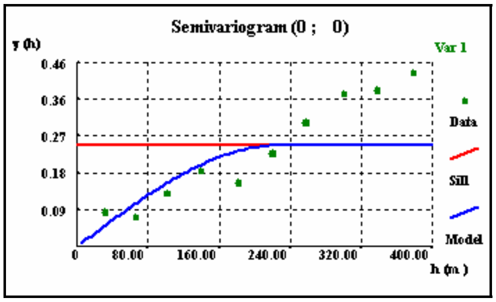

Fig.27 – Variogram of indicator variable for As>=20mg/kg (in [2])

Indicator kriging parameters obtained by variogram modelling are presented in below (table 1)

Table 1 – Variogram and kriging parameters

| Range distance (m) | Nugget effect (C0) | Sill (C0 + C1) | Model |
|---|---|---|---|
| 225 | 0 | 0.25 | spherical |

Figure 28 illustrates a probability map for the occurrence of arsenic in soil, in concentrations higher than 20 mg/kg, modelled during the exploratory site investigation phase.

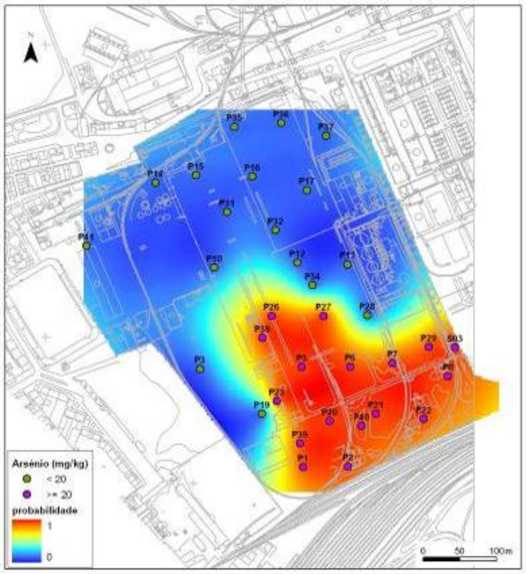

Fig.28 – Probability map for As higher than 20mg/kg (in [2])

Figure 29 presents the morphology of the contaminated area, for arsenic grades above 20mg/kg.

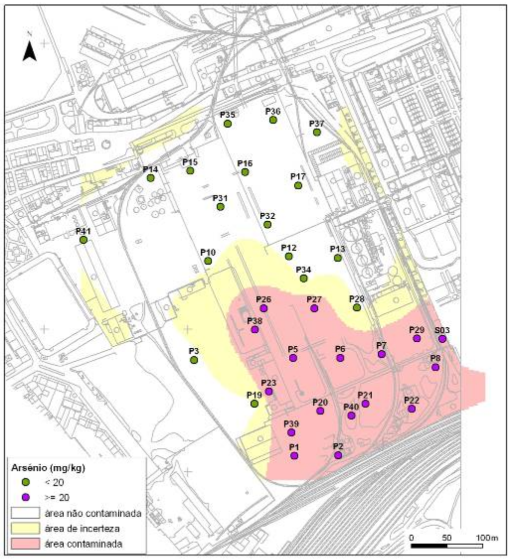

Fig.29 – Morphology of contaminated areas in As (in [2])

Studies showed that contamination is closely related with the presence of the wastes dumped by the old industrial units, such as those from the pyrite *ustulation* (a incineration process) and metallurgical processes, rich in heavy metals, namely Cu, Zn, Pb, and also in As. Consequently, the higher concentration values were identified in the southern part of the industrial area, in an extension of about 30% f the studied area, as illustrated in figure 30.

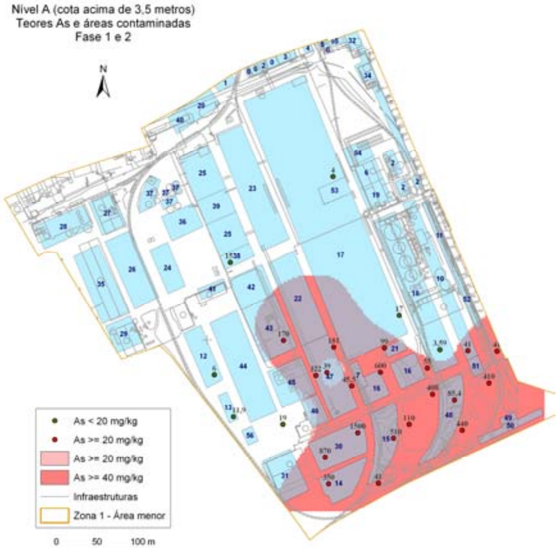

Fig.30 – Contaminated areas and location of industrial plants (in [2])

The contamination model was built using GIS to integrate estimated contaminated maps for two depths, with soil properties, such as clay content, as shown in figure 31.

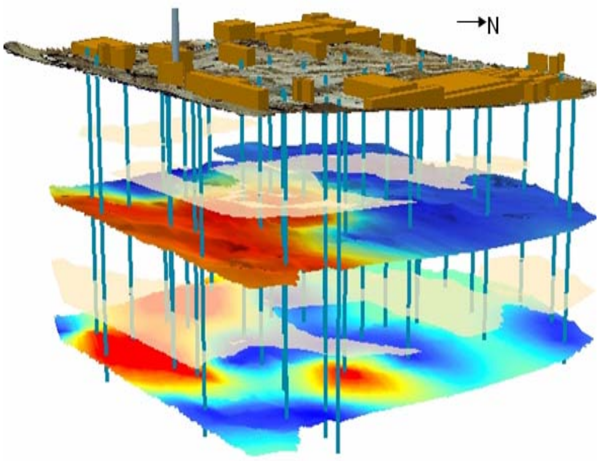

Fig.31 – 3D contamination model (in [2])

Groundwater site model was built with *Visual Modflow* software [7], based on estimated hydrogeological units (fig. 32).

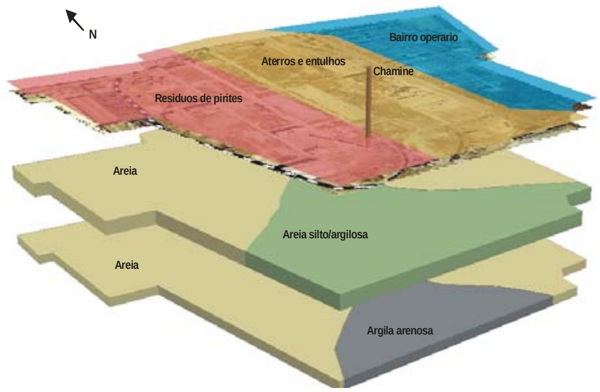

Fig.32 – Hydrogeological units estimated by indicator kriging. Top layer: industrial waste (in [2])

Figure 33 illustrates the 3D hydrogeological model, built with *Modflow* software [7].

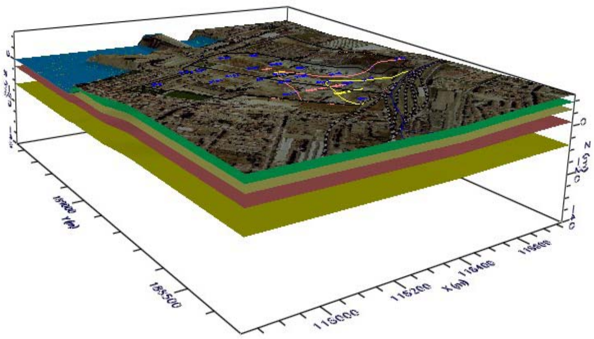

Fig. 33 – Hydrogeological model

Figure 34 shows the simulation of local groundwater flow as well as particles pathways, based on local aquifer characteristics

Fig.31 – Dynamics of local groundwater flow and path of a contaminated plume (in [2])

As it can be seen, the groundwater flow is rather low, weakening the spread of the contaminated plume towards the Tagus estuary, due to the low gradient values and tide influence, which means that the mobility of chemical elements could be mainly dependent on the physical and chemical properties of the pollutants and the media.

## 3 Conclusions

The application of a three phased methodology for site investigation and the integration of geostatistical models in each phase allowed: (i) the rationalisation of site investigation works at different stages; (ii) the characterisation of pollutants in the environment; (iii) the estimation of contamination plumes in soils and groundwater and respective volumes for treatment; (iv) the definition of the local contamination model in order to develop a risk analysis approach for urban occupation.

Environmental requalification of the polluted industrial area encloses the need of a risk analysis evaluation approach in order to define the best remediation actions for minimizing potential contamination risks facing to a future urban occupation [8].

## 4 Acknowledgments

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