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Upgrading groundwater quality using spatial assessment of pollution impacts on soil resources in Tagarades area, Greece.

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ABSTRACT
Gourd water quality is heavily dependent on overlying soil resources. To prevent groundwater contamination, a set of measures should be taken toward the overlying soil physical and chemical properties especially when a threat of heavy metal pollution is involved. Landfill leachates are one foremost source of soil and groundwater pollution. In 2006, a fire broke up in the landfill located in the Prefecture of Thessaloniki, in North Greece in the municipality of Thermi. The barriers of the lagoon collapsed and more than 1000 m^3 of leachates were released into a local stream and spread around to an area of 500 ha. The affected area is mainly used for agricultural purposes, irrigated and non-irrigated annual crops. The objectives of the study are firstly to assess the level of soil resources degradation and secondly to determine the spatial risk of metal mobilization and the possibility of groundwater pollution. A number of 40 soil samples taken from different soil horizons were tested for contamination and the total extractable concentrations of heavy metals were screened. The analysis detects seven different heavy metals in the study area namely: **As, Pb, Cd Zn, Cu, Mn** and **Ni.** The threat of having heavy metals contamination is proportionally increasing with soil depth and the accumulation of heavy metals in the soil. Using Geostatistical analyst under ArcGIS environment is essential to determine spatial variability in the content of heavy metals in soil to be cost effective tool of spatial remediation techniques.

1. INTRODUCTION

Soil has always been important to groundwater quality, providing a resource that can be used for different purposes. Groundwater significantly influences a variety of functions such as plant growth and the cycling of water that sustains the human population (D'Emilio *et al*., 2006). Heterogeneity is an inherent property of soils; therefore in a natural landscape, it represents a wide variety of soil attributes in terms of spatial and volumetric issues. The interactions of the soil format processes affect consequently the quality and the quantity of groundwater (Shi *et al*., 2006).

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Understanding soil quality means assessing and managing soil so that it functions optimally now and is not degraded for future use. The ultimate purpose of assessing soil quality is to provide the information necessary to protect and improve long-term agricultural productivity, groundwater quality, and habitats of all organisms including people (Thornton *et al*., 1994).

Pollution is a common concern in many modern, industrialized urban communities around the globe (Moon *et al*., 2000; Zhang *et al*., 2002). The connection betwee3a

n soil pollution and various groundwater contaminations is now well recognized and reasonably well identified by the general public (Romic and Romic, 2003). Soils are usually the interface between human activities and conserved groundwater beneath that should be preserved and protected (Krzyztof *et al*., 2004). The main sources of heavy metal pollution are: smelters, metal processing works, power plants, refuse incinerators and emissions derived from motor vehicles. Significant contributions are also made by chemical manufacturing, oil refineries, metal processing and plating, tanneries and fertilizer manufacturing industries (Tiller, 1989).

Lanfill leachates are considered to be among the most serious threats of soil and groundwater resources. Threats to the groundwater from landfills leachate exist where the hazardous industrial waste is also co-disposed with municipal waste and no provision of separate secured hazardous landfills exists. The leachate is still reported as a significant threat to the groundwater (Lee, 2002). A number of incidences have been reported in the past, where leachate had contaminated the surrounding soil and polluted the underlying ground water aquifer or nearby surface water (Lo, 1996; Masters, 1998; Kumar *et al*., 2002).

The way that a landfill has been constructed determines the level to which there is a risk of groundwater pollution by the leachates. In landfill sites which have been created recently, liners are presented and this greatly limits the leachate leaking and the only way it will leave the cell is if the liner tears. In the context of environmental issues, risk is defined as the probability of occurrence of a particular adverse effect on human health or the environment as a result of exposure to a hazard, which may be a hazardous chemical in the environment, a natural hazard, or a hazardous technology (Schierow, 2001).

The current research focuses on issues related to groundwater contamination resulting from soil pollution. The problem that will be addressed is the pollution of soil resources by heavy metals in the area of Tagarades due to the leakage of landfill leachates. The objectives of this study are: a) – assess the level of soil resources pollution, and b) - determine the risk of metal mobilization and the possibility of groundwater pollution.

The results of the study in terms of data and thematic maps are expected to provide the scientific basis for sustainable management of the area and the establishment of a remediation program in the near future to prevent groundwater contamination through preparing restoration measures to reveal the impact of soil heavy metal pollution caused by leakage of landfill leachates.

2. Materials and Methods

2.1. The study area

The size of the study area is about 500 ha located in the Prefecture of Thessaloniki, in North Greece and more specifically in the municipality of Thermi between the villages Trilofos, Agia Paraskevi, and Tagarades. The study area is shown by satellite, orthoectified image in Fig.1.

The leachates of the landfill are collected in a lagoon next to the landfill. In 2006, a fire broke up in the landfill and the barriers of the lagoon collapsed. More than 1000 m^3 of leachates were released into a local stream and spread around to an area of 500 ha, the leachates remained for approximately 10 months, as many land owners reported. The affected area is mainly used for agricultural purposes, irrigated and non-irrigated annual crops, while several residencies are also found in the area. The agriculture practices comprise olives cultivation as well as annual crops.

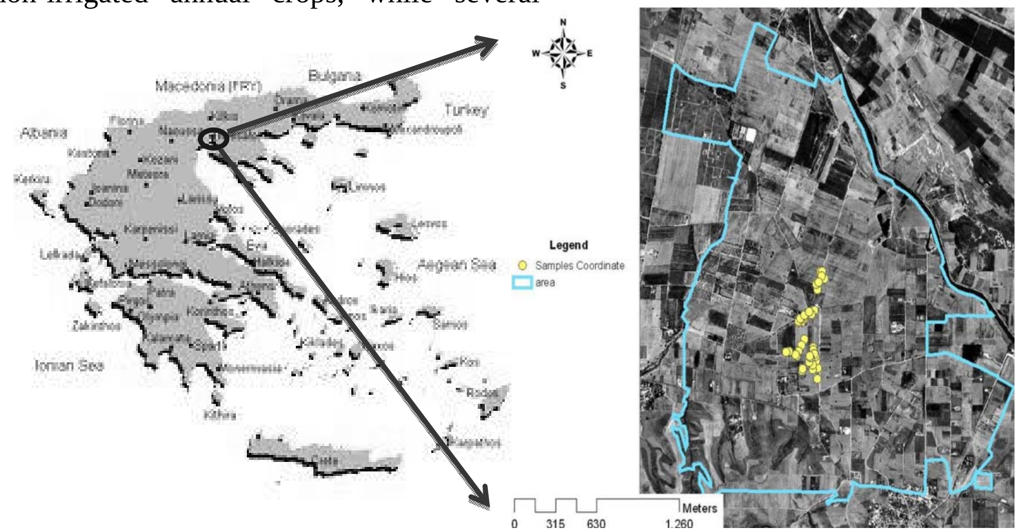

Fig. 1: Location of study area and soil sampling in Tagarades, Greece

2.2. Soil analyses

A number of 40 soil samples were taken from the study area representing the affected area by the leachates. The location of the soil samples that were allowed to be taken by land owners are demonstrated in Figure 1. The sampling started in September 2007 and lasted for two months. Soil samples were taken from light depth (0 – 100 cm) representing the three different soil horizons A, B and C (A = 0 – 30, B = 30-70 and C= 70 – 100 cm).

Atomic Absorption Spectrophotometer was used to detect total extractable heavy metal concentration of seven different heavy metals in the 40 soil samples of the Tagarades area. These metals are: **As, Pb, Cd Zn, Cu, Mn** and **Ni**. The analyses were carried out after Lindsay and Norvell (1978) and USEPA (1983), using a Perkin Elmer 2100 Atomic Absorption Spectrometer. Furthermore in each sample the pH, clay content, and organic matter were measured using standard methods of soil analysis (ASA-SSSA 1996, 1986), as parameters affecting the mobility of heavy metals.

2.3. Geostatistical analyses

The spatial variability of heavy metal content in soils was determined by means of geostatistical methods in which semi-variance is the basic function ($\gamma(k)$) defined as the square of the difference between a soil property in point Xj and the same property in a point at a distance of $xi+k$ (Warrick *et al*., 1986; Komisarek, 1994). There are four types of geostatistical analyses, each of which is valid for a certain analysis condition or complex of conditions. To compare these models statistically, the Root Mean Square Error (RMS) would be implemented. The smaller the root mean square, the closer the model comes, on average, to predicting measured values that were removed from the analysis. The adopted geostatistical method is Inverse Distance Weighted due its RMS values.

Inverse Distance Weighted (IDW) is deterministic interpolator, the interpolation implements anchored in the basic law of geography features that are close to one another are more alike than features that are far apart.

2.4. Calculations

Spatial distribution

$$\gamma(k) = \frac{1}{2 * n(k)} * \sum_{i=1}^{n(k)} [Z(xi) - Z(xi+k)]^2$$

Where: *n(k)* - number of pairs of observation; *Z(xi)* - soil property measured in point *x*, and in point *x* + *k*.

Interpolation equation

$$Z * (xo) = \sum_{i=1}^{n} \lambda i * Z(xi)$$

Where: *Z* * (*xo*) - interpolated value of variable *Z* at location *xo*, *Z*(*xi*) - values measured at location *xi, λi*; - weighed coefficients calculated on the basis of the semivariogram when:

$$\sum_{i=1}^{n} \lambda i = 1$$

The weights, calculated in this way, make it possible to obtain non-biased interpolated values that is, the expected value: *E[Z*(xo) - Z(xo)] = 0* and the estimated variance Var. [*Z*(xo) - Z(xo)*]= minimum.

Trend and random error

$$Z(s) = \mu(s) + \varepsilon(s)$$

The symbol s stands for the location of the prediction location. (Representing a pair of x,y coordinates. *Z(s)* is the variable you are predicting (total extractable heavy metal concentration). *μ(s)* is the deterministic trend. *e* (s) is the spatially auto-correlated random error.

In order to reclassify the prediction risk maps into four classes (Low, Moderate, High and Severe) according to their total extractable concentrations, natural breaks classification method is the adopted method (Fig. 3). Natural Break is the default classification method that uses an algorithm called “Jenks Optimization” (ESRI, 2008). The algorithm is based on minimizing the sum of squared deviations from a class‘s means through forming groups that are internally homogenous but maintaining heterogeneity between classes, resulting in classes of similar values separated by breakpoints. This method works well with data that is not evenly distributed and not heavily skewed toward one end of the distribution.

To predict the overall risk of heavy metal pollution, the study requires an approach to identify parametric values in modeling the risk of pollution. Weight in Spatial Decision Support System (SDSS) provides the weight that the study implements to proceed with Weight Linear Combination (WLC) (Elhag, 2008). The relative toxicity of each heavy metal risk (Rank) is following Robert (1999) according to the tested heavy metal lethal douse.

Weight Linear Combination formula

$$WLC = \sum wixi * \Pi cj$$

Where *Wi* = weight of factor *I*, *Xi* = criterion score of factor and, *Cj* = criterion score of constraint j

3. RESULTS AND DISCUSSION

To explore the extent of heavy metal tendency to pollute underground water of the Tagarades area, the samples were tested for total extractable heavy metal concentration in different soil depths down to 100 cm (Horizons A, B and C). The general pattern of the heavy metals mobilization in the tested soil varies according to the tested metal. Statistically, all the heavy metals show significant decrease in their total extractable concentration across soil profile except those of **As** and **Zn** in terms of R^2 values. The former two heavy metals had values of 0.661 and 0.511 respectively, while the remaining heavy metals had R^2 values above 0.9 (Fig. 2).

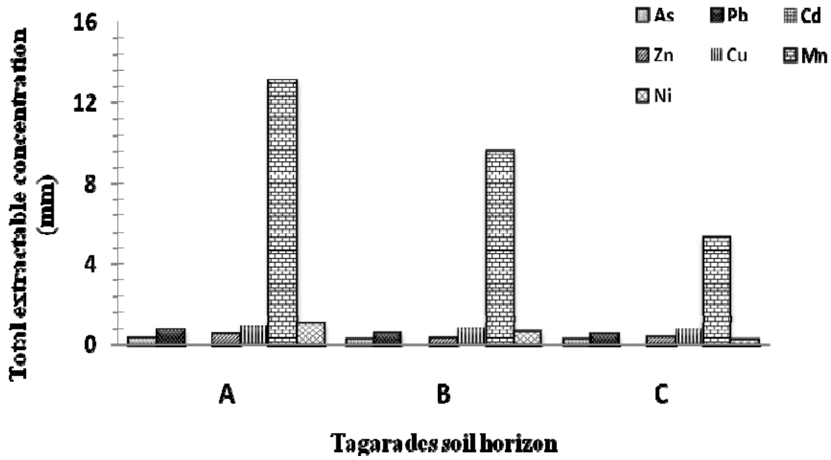

Fig. 2: Total extractable concentrations of different heavy metals in Tagarades soil horizons

The detected heavy metals fall into two categories based on the heavy metals mobility in the tested soil. The first category includes As, Pb, Cd, Zn and Cu. This heavy metal category tends to accumulate in Tagarades soil at a depth of 100 cm. More than 50 % of these heavy metal total extractable concentrations are found at a depth of 100 cm as calculated to be as the following: 52.6, 67.8, 67.9, 69.2 and 81.8 % for Cd, Cu, Pb, Zn and As respectively. On the other hand, the second category includes only Mn and Ni. The total extractable concentrations were considerably low and measured 28.6 and 38.9 % for Ni and Mn, respectively. The detected total extractable concentrations of the tested heavy metals are lower than the maximum allowable values of heavy metals in soil used in neighboring countries based on the Common Ministerial Decision (1991).

Metal interactions in soils vary considerably with the nature of soil types. The mobility and the fate of metals is determined by the nature of the metal species, their interaction with soil colloids, soil characteristics and duration of contact with the surface binding these metals. Soils of Tagarades with slightly high pH (Fig. 3), moderate organic matter content (Fig. 4) and low clay (Fig. 5) are affecting availability and mobility of the heavy metals by controlling the speciation of the elements, temporary binding by particle surfaces (adsorption-desorption processes), precipitation reactions and availability in soil solution. Both the concentration of trace metals and their speciation vary significantly with the composition of soil solution and the amount of moisture present in the soils (Fotovat *et al*., 1997). The different amount of metals retained by different soil types may be attributed to the different clay content and mineral composition of the soils, their pH, organic matter content and soil solution composition which is the medium of reaction in soils.

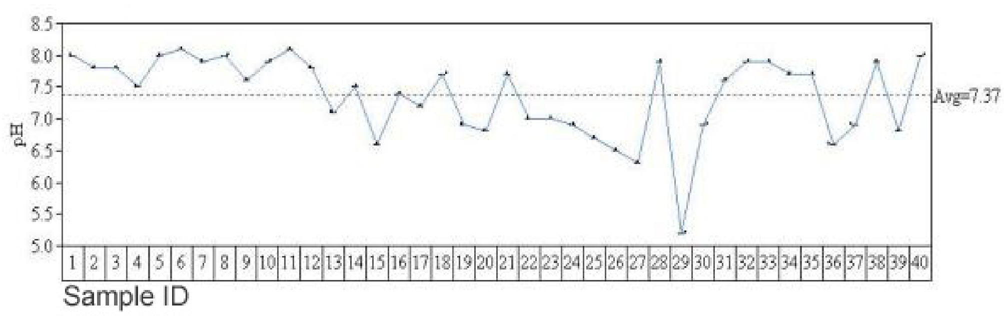

Fig. 3: Tagarades soil pH

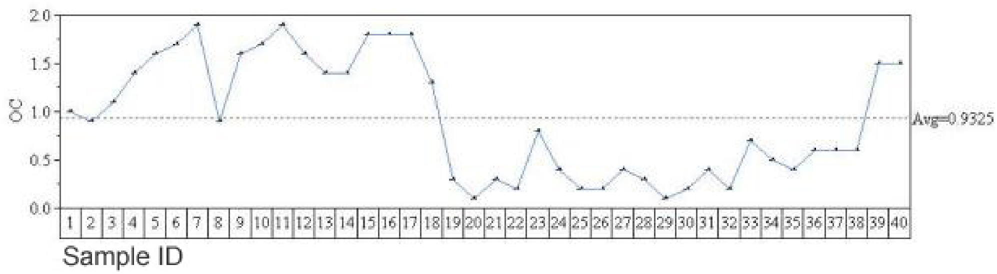

Fig. 4: Tagarades soil organic carbon (%)

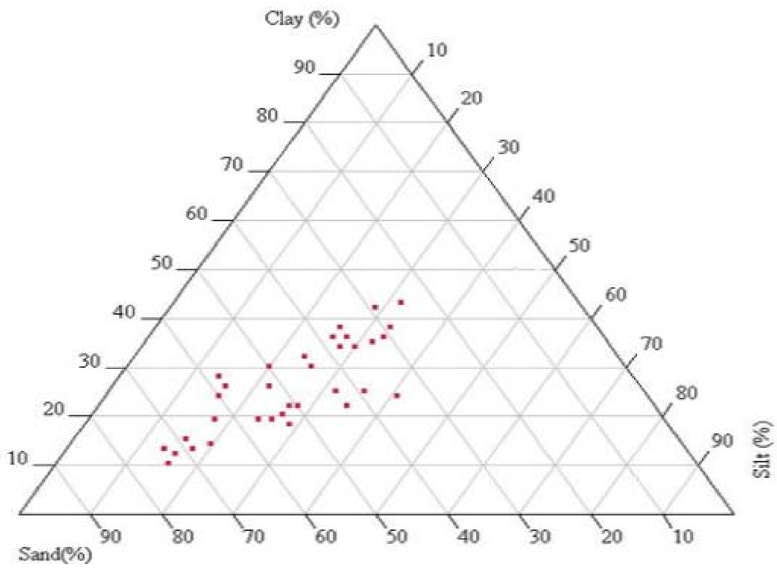

Fig. 5: Soil textural classes in Tagarades area

Consistent with the Cross Validation Method to evaluate different interpolator accuracy, Inverse Distance Weighting interpolator was the adopted method for statistical reasons, as it has the lowest Root Mean Square Error (RMS). RMS was calculated to be 0.0146, 0.0151, 0.0153 and 0.0154 for Inverse Distance Weighting, Global Polynomial, Local Polynomial and Kriging respectively for **Cd** heavy metal total extractable concentration as it has the most homogenous data distribution in terms of lowest standard deviation and lowest Skewness value.

The buffer zone of e predicted values meant to be with 250 m surrounding the tested sites (Fig.6), the extent of the buffer zone was based on the maximal heavy metal mobility in most favorite soil following Grathwohl *et al*. (2003).

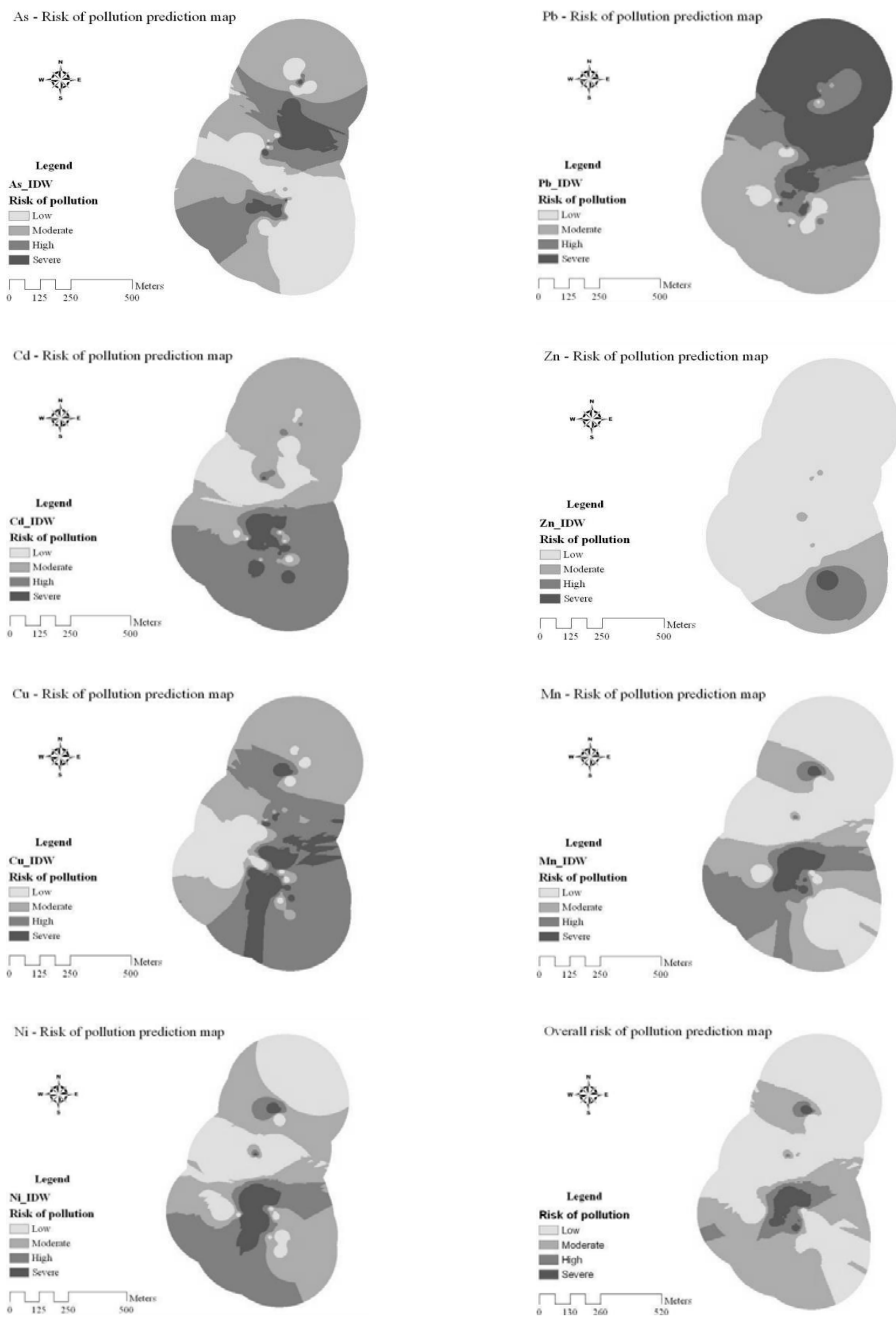

Fig. 6: Risk of pollution prediction maps and overall risk in Tagarades soil

4. CONCLUSION

The group of the heavy metals containing Arsenic, Lead, Cadmium, Zinc and Copper does not drop dramatically through the soil profile as the lowest element was Cadmium and its total extractable concentration remains above 50 % at the depth of 100 cm of its initial maximum concentration at soil surface. Furthermore, the loss of the total extractable concentration of Arsenic through soil profile was only about 18 % of its initial maximum concentration. This means that the corrosion products of these heavy metals leach through Tagarades soil profile and there is a great risk of these metals contaminating Tagarades underground water.

Consequently, in winter time and the rainy season, groundwater level would rise up and become closer to the soil surface through water capillary suction, thus maximizing the possibility of the metal corrosion products being transported through the groundwater flow. In this case, there is a great risk of heavy metal contaminations spreading out to the groundwater and soil profile far away from the contaminated sites through the groundwater flow. Moreover, because clay has the property of high horizontal but low vertical permeability, the metal downward movement is slower than the parallel one. Another obsession calls for notice is at Tagarades soil, the underground water flow will accelerate the metal horizontal transportation, which will be non source of contamination extents further from the original polluting point.

According to the heavy metal spatial distribution and overall risk prediction map, agriculture practices should be halted according to the overall risk map at the severely polluted sites till the proper remediation techniques take place. The results of the current study in terms of multivariate analyses, thematic maps and risk assessment are providing the scientific basis for sustainable management of the area and the establishment of a remedial program in the near future to improve soil quality following the preparation of restoration measures to reveal the impact of soil heavy metal pollution caused by the leakage of the landfill leachates. In idiom of advantages and disadvantages of the different remediation techniques and according to the nature of the Tagarades soil, the phytoremediation technique is the most favored and also the least costly. The use of metal-accumulating plants to remove pollutants from soil and water contaminated with toxic metals is the most rapidly developing component of this environmentally friendly and cost-effective technology and can be effectively applied in the area of Tagarades.

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