Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.983988

57 (2016) 2982–2995
February

Taylor & Francis
Taylor & Francis Group

Geostatistical estimation of risk for soil and water in the vicinity of olive mill wastewater disposal sites

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Received 6 October 2014; Accepted 29 October 2014

ABSTRACT

Olive mill wastewater (OMW) is often disposed of in poorly engineered evaporation ponds or various environmental receptors in most Mediterranean countries causing contamination of soils and water bodies. The aim of this work is to estimate the risk for soils and waters as a result of OMW disposal in an area of 15 km^2 at Rethymnon, island of Crete, Greece. Soil, surface, and groundwater samples were collected over a period of five years and geostatistics using the kriging approach was considered for the assessment of risk. Risk maps for several pollutants, namely phenols, Ni, Cr, and available P, in soil and water were produced. The results of the study indicate the presence of hot spots in the area under investigation, mainly in the vicinity of OMW disposal sites. Finally, the fate of contaminants in affected media is discussed and a framework for monitoring of soils and water bodies in areas affected by OMW disposal is proposed.

Keywords: Olive mill wastewater; Geostatistics; Risk; Soil; Water

1. Introduction

Olive mill wastewater (OMW) is the main waste that is generated during the olive oil extraction route. It is a dark, turbid, easily fermentable, and foul-smelling liquid, while its characteristics depend mainly on the extraction method used, the variety and ripeness of olives, the soil type (e.g. sandy loam or loamy sand), and the climate. It has slightly acidic pH (4.5–5.5), high electrical conductivity (EC) (3.5–12.5 dS/m), COD/BOD ratio up to 2.5, and high organic content that may exceed 140 g/L [1,2].

The annual OMW generation in the Mediterranean countries exceeds 3×10^7 m^3. An average mill produces daily around 15 m^3 during the operating period between November and March each year, while it is estimated that the generated volume of wastewaters for each ton of produced olive oil may vary between 3.25 m^3 for the traditional (pressure type) and 5 m^3 for modern (centrifuge type) mills, respectively [3,4].

OMW management is usually improper, causing noticeable environmental problems. The most common management options in the Mediterranean region

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include disposal on soil and in evaporation ponds. In the second case, a neutralization step may be included, but it has to be mentioned that evaporation ponds rarely meet engineering criteria in terms of stability and control of leachate migration, thus increasing the risk for groundwater and soil contamination in most cases. It is estimated that in Greece, over 1 million m^3 of OMW are discharged annually in streams, rivers, and bays. The utilization of OMW for the production of oil preservatives, fat, or fermentation products is a challenge but it is very rarely attempted [5].

An alternative management option, which is considered in almost all Mediterranean countries, is the use of OMW as fertilizer or for irrigation of soils. Several studies have been carried out to assess the impacts on soil and water as a result of this practice. Disposal of OMW on soils can affect soil chemical and biological properties, including texture, pH, conductivity, aggregate properties, content of organic matter, available P and K, hydrophobicity, and soil microbial communities, as well as water retention, infiltration rate, and crop yield. Detailed studies need to be carried out to assess all these short and long term impacts on soil and subsequently on groundwater, and thus identify the optimum OMW application rates in each case [6–12].

Risk assessment studies are often carried out to assess the quality of various environmental receptors, including soil and water (surface and groundwater) [13–15]. The assessment of the degree of soil and water contamination in the vicinity of OMW disposal sites and, thus, the estimation of risk for each affected body depends on a number of factors such as volume, frequency, and duration of wastewater discharged, soil type, land use, presence of aquatic streams, depth of aquifer, precipitation rate, as well as mobility, and fate of contaminants [16,17].

In geosciences, geostatistics provides a coherent set of probabilistic techniques aiming to the spatiotemporal mapping of regionalized variables. The problem of local estimation is to find the best estimator of the mean value of a random field (RF) over a limited domain, the dimensions of which are small compared to the dimensions of the quasi-stationary (homogeneous) zones of the study area. The available information used for local estimation within the quasi-stationary zone is generally made up of a set of data (e.g. core measurements) and structural information (e.g. the covariance model characterizing the spatial variability in the studied zone). Kriging is a local estimation technique which provides the best linear unbiased estimator of the unknown characteristic studied. This limitation to the class of linear estimators is quite natural, since it means that only the second-order moment of the random function (i.e. the covariance or variogram) is required, and, in general, it is possible in practice to infer the moment. A covariance model is adjusted to experimental covariance by means of a fitting operation. Ordinary kriging is characterized by a measure of its accuracy, which is the estimation error variance. This is useful to define estimation uncertainty and to outline areas that need a supplemental sampling [18,19].

Geostatistics can be used to accurately assess risk in contaminated sites. The approach used considers the value of a parameter or the concentration of a contaminant in an affected medium as a regionalized variable in space and time. The variable is then modeled as a RF [20]. Starting with the calculation and modeling of the covariance or variogram function, it attempts to estimate the value/concentration of a parameter in non-sampled areas using kriging and to mathematically express the statistical errors. The accuracy of geostatistics depends on several parameters including the methodology used, the number of samples in each area or affected medium, the frequency of sampling, the area covered, and the presence of hot spots, but is also affected by other exogenous factors such as the climate and the potential transformation of contaminants over time. This accuracy may be further improved if the uncertainty of the measurements is incorporated into the mathematical model [21]. Finally, what is also important in a risk assessment exercise is the identification of potential hot spots which may cause spatial trends in the mean value of the RF and result to a non-Gaussian data distribution [22–25].

In international literature, there are many examples considering the use of geostatistics to assess risk for soils and waters in waste disposal sites or in the vicinity of industrial sites [26–31]. To our knowledge, this is the first attempt to use geostatistics and estimate risk for both soil and water in the vicinity of an OMW disposal site.

2. Description of the study area

The area under study is in the Municipality of Rethymnon, in the island of Crete, Greece; North latitude is 35˚17´ and East longitude is 24˚21´. The area has subtropical Mediterranean climate and is characterized by mild winter and dry-hot summers. The annual temperature varies between 8˚C in February (mean min. temperature) and 28˚C in July (mean max. temperature). Average precipitation is 692 mm and most of it is recorded between October and April each year, whereas almost no precipitation is recorded during summer.

The geology of the wider area includes loose Quaternary deposits (alluvial deposits, slope debris and fans, and torrent terraces), Neogene deposits (limestones, conglomerates, sandstones, and clays), tectonic covers of Pindos and Tripolis geotectonic zones consisting of limestones and marbles (plattenkalk, dolomites, and undivided carbonated formations), flysch, and metamorphic rocks (phyllites, quartzites, shales, schists, and meta-sandstones), and ophiolites of the autochthonous Ionian zone. Soils are slightly or moderately alkaline, rich in carbonates, and have clayey or silty clayey texture [32].

Groundwater is the main water supply and irrigation source that comprises 82% of the total water consumption in the area. The major parameter that affects surface water potential is the geomorphology of the island. Thus, the main mountainous terrains which have been developed along the central zone influence the formation of many ephemeral rivers. The total annual surface water potential is estimated at 1.3 km^3/y [5].

Olive oil production, using mainly three-phase continuous centrifuge systems, is the main activity in the area under study for many centuries. Nowadays, two olive oil mills are in operation in the area under study for more than 14 years. It is mentioned that in Greece as well as in most Mediterranean countries, olive mills are scattered and have rather small capacity since they are family businesses. OMW produced are disposed of mainly in evaporation ponds constructed with native soil and simple engineering, while no impermeable membranes or other protective media are used.

The largest site (AC-1) in the area under study has an area of 1 ha with almost 5% slope in which two operating OMW disposal ponds are present with dimensions of 30 × 44 × 2 m (main disposal pond) and 32 × 20 × 3.5 m (auxiliary disposal pond). Another operating pond with dimensions of 39 × 10 × 1.7 m is located in another site (AC-2) in the wider area, at a distance of ~4.2 km from AC-1. In Fig. 1, a Google map including AC-1 and AC-2 disposal sites is presented. It is also mentioned that three abandoned, for more than 11 years, OMW disposal ponds are also present in the wider area under study at a distance varying between 2.5 and 4.5 km from AC-1.

3. Methodology

3.1. Soil sampling

The area under study is 15 km^2 and includes AC-1 and AC-2 sites. Thirty sampling points were identified to assess the effect of uncontrolled OMW disposal on agricultural soils and subsequently on water. Soil sampling points were carefully selected by considering the location of evaporation ponds as well as the topography, the geomorphology, and the activities carried out in the area under study. A total of six soil sampling campaigns were carried out within the period May 2009–2010. Over 1,200 soil samples were collected from the pond walls, the soil surface (0–15 cm), and various depths (up to 175 cm using 25 cm intervals) during the entire sampling period. Control samples were collected from points located away from the evaporation ponds. The sampling density was two samples/km^2. Duplicate samples were taken from all sampling points during each sampling campaign.

For the geostatistical analysis and the production of risk maps, the average concentration of phenols, available P and Ni in surface soil samples collected from 11 selected sampling points, located in AC-1 and AC-2 sites was considered. Phenols are the main constituent of OMW, while available P is a nutrient and Ni in high concentrations can be a contaminant that affects soil quality and plant growth. Other parameters could have been selected, but no additional information would have been provided since the trend of almost all parameters is similar in the area under study. In Table 1, the coordinates (using the World Geodetic System, WGS 84), the description, and the distance of each sampling point from the main active evaporation pond are presented.

Soil analysis was carried out using standard methodologies [33,34]. The most important parameters measured are pH, EC, phenols, available P and K, and concentration of Fe, Cd, Cu, Pb, Zn, Mn, Ni, Mo, and Cr. Heavy metal concentrations in soils were determined by a flame atomic absorption spectrophotometer (Perkin Elmer Analyst 100, USA) using a furnace when required.

3.2. Water sampling

In order to evaluate the quality of the existing water bodies and assess quantitatively the risk in the area under study, water samples have been collected during the period May 2009–June 2014 from 11 water sampling points and five piezometers installed in drillholes, in the wider area under study (Fig. 2). The sampling points included surface streams, springs, water supply pipes, and old wells. It is mentioned that 26 water sampling campaigns were implemented during the period May 2009–June 2014. Piezometers were sampled during the period January 2011–June 2014 in which 16 sampling campaigns were carried out. The sampling density for water samples was one sample/km^2. The description, the location, and the distance of all water sampling points including piezometers, from

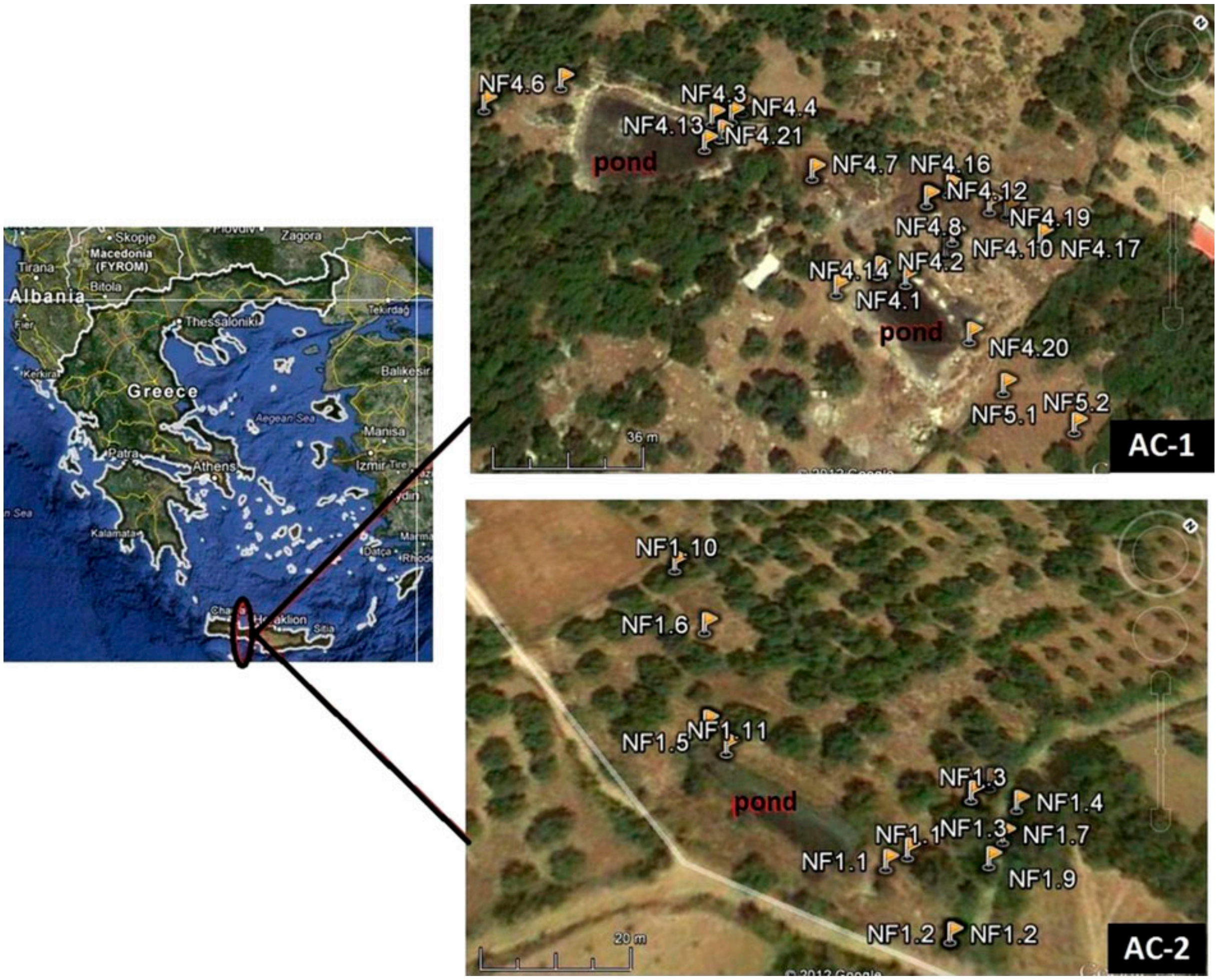

Fig. 1. Google map of the sites AC-1 and AC-2 (up and down, respectively); flags represent soil sampling points.

the main disposal pond in AC-1, are shown in Tables 2 and 3.

The criteria used for the selection of water sampling points were based on the hydrography, geology, and geomorphology of the area. It is mentioned that one of five piezometers has been considered as control and is located in a distance of 537 m from the main disposal pond in AC-1. The location for the installation of the piezometers was carefully selected by considering the location of the evaporation ponds on a slope, the morphology of the area, the direction of overflow from the ponds, and the movement of soil (pore) water. Thus, drillholes were drilled on an imaginary line connecting the main pond and the nearby provincial road, since leachates and OMW disposed uncontrolled on soils or as a result of overflow from the ponds would move to this direction. Duplicate samples were taken from all sampling points during each sampling campaign.

The parameters measured *in situ* include pH (using a pH5 Meter LaMotte 5 Series) and EC (using a CON5 Meter LaMotte 5 Series). Other parameters determined include phenols, total hardness, NO_3^-, SO_4^{2-}, PO_4^{3-}, and elements such as Ni, Cr, Mn, Cl, K, Fe, Cu, Pb, Cd, Mo and Zn using a LaMotte Smart2 [1919-EX2] colorimeter, a Perkin-Elmer Analyst 100 atomic absorption spectrophotometer, or inductively coupled plasma mass spectrometry (ICP-MS, analyzer Agilent Technologies 7500cx).

For the geostatistical analysis and the production of risk maps, the average concentration of phenols, Cr and Ni, in all water samples was considered.

3.3. Geostatistics

Geostatistics, which is particularly suited to the study of natural phenomena, is the most appropriate tool for further processing of the above data [20].

Table 1
Selected soil sampling points in the wider study area

Soil sampling point	Description	Longitude/ latitude (WGS 84)	Sampling depth (cm)	Euclidean distance (m) from the main disposal pond in AC-1
NF4.1	Upstream of the small pond (AC-1)	533345/3907126	0–25, 25–50, 50–75, 75–100	51.9
NF4.2	Inside wall of the small pond (AC-1)	533350/3907137	0–25, 25–50, 50–75	55.2
NF4.4	Outside wall of the large pond (AC-1)	533290/3907142	0–25, 25–50, 50–75, 75–100, 100–125, 125–150	6.8
NF4.6	Upstream of the large pond (AC-1)	533247/3907116	0–25, 25–50	51.6
NF4.7	Downstream of the large pond (AC-1)	533318/3907145	0–25, 25–50, 50–75, 75–100	25.2
NF4.10	Downstream of the small pond (AC-1)	533358/3907158	0–25, 25–50	67.3
NF4.12	~60 m distance from the large pond (AC-1)	533346/3907161	0–25	57.2
NF5.1	Downstream (7 m) of the small pond (AC-1)	533394/3907137	0–25, 25–50, 50–75	99.8
NF5.2	Downstream (25 m) of the small pond (AC-1)	533414/3907142	0–25, 25–50	119.9
NF1.1	Downstream from the pond (AC-2)	537370/3908490	0–25, 25–50, 50–75, 75–100	4,294
NF1.5	Inside wall of the pond (AC-2)	537330/3908482	0–25, 25–50, 50–75	4,254
NF7.1	Control	533392/3906608	0–25	537

Fig. 2. Location of water sampling points in the study area (blue flags: area A) and drillholes 1–5 (green flags: area B); orange flags represent soil sampling points.

Using the available measurements for pollutant concentrations as well as the described structural models, concentration maps for surface soils (sampling depth 0–25 cm) and water were produced for each pollutant. Existing thresholds (Greek, Canadian, WHO, and several European Directives) for soils and waters have been considered. All maps were produced using the kriging approach.

In the concentration maps shown in the next section, the color shows the intensity (magnitude) of the parameter; the darker the color, the higher the value. Axes X and Y of the concentration maps show the coordinates according to the WGS 84. As mentioned before, the area covered in the concentration maps is 15 km^2.

4. Results and discussion

4.1. Soil and water analyses

Table 4 shows the ranges of values of selected parameters determined in (i) waters collected from

Table 2
Description and location of water sampling points

Sampling point	Description	Longitude/latitude (WGS 84)	Euclidean distance (m) from the main disposal pond in AC-1
W1	Old well 1 in "Agios Konstantinos" village (depth of water table 3–6 m)	533234/3906428	711
W2	Old well 2 in "Agios Konstantinos" village (depth of water table 3–6 m)	533413/3907715	590
SKV	"Kato vrisi" spring	533353/3905502	1,636
SSo	"Sotira" spring	533650/3904915	2,250
SR	Spring in central square of "Roustika" village	533928/3904582	2,632
SSa	"Saitoures" spring	534970/3903775	3,756
IP1	Water supply pipe 1	534838/3903811	3,667
IP2	Water supply pipe 2	533120/3904053	3,089
SM	"Moundros" spring	533352/3903551	3,586
PM	"Moundros" pool	533352/3903551	3,586
RB	Stream located between "Agios Konstantinos" and "Agios Andreas" villages	533935/3907705	856

Table 3
Description and location of the piezometers installed in drillholes

Piezo-meters	Description	Longitude/latitude (WGS 84)	Euclidean distance (m) from the main disposal pond in AC-1
1	At AC-1 disposal site, near the small disposal pond (15 m depth)	533360/3907154	67
2	In AC-1 disposal site, near the large disposal pond (24 m depth)	533319/3907145	25
3	Control (40 m depth)	533354/3906603	537
4	Downwards AC-1 disposal site (22 m depth)	533443/3907161	150
5	In the vicinity of the stream RB (see Table 2) (25 m depth)	533884/3907710	822

surface streams, springs, water supply pipes, old wells, and piezometers installed in drillholes and drinking water standards (mg/L), in (ii) soils (mg/kg) collected in the study area as well as the Canadian thresholds for agricultural soils.

It is seen that water samples are characterized by neutral to relatively alkaline pH varying between 6.5 and 8.9. EC ranges between 92–2,480 μS/cm and total hardness between 130 and 431 mg/L $CaCO_3$.

The concentration of phenols, for which no health-based thresholds have been proposed, reaches higher values for the water samples collected from W1, SKV, and SSo. An indicative acceptable value of 0.5 μg/L is proposed for phenols by the Greek Common Ministerial Decision [35]. High phenol concentrations (up to 3 mg/L) have been also detected in piezometers 1 and 2 which are located close to the evaporation ponds in AC-1 and are due to the seasonal release of OMW, usually during spring, from the large evaporation pond.

The concentration of NO_3^-, SO_4^{2-}, PO_4^{3-}, Cl, Fe, Cu, Zn, and Mo are lower than the respective drinking water standards, as shown in Table 4. The concentrations of K, Ni, Cr, and Mn (up to 230, 0.1, 0.62, and 1.2 mg/L, respectively) exceed threshold values. All these high values are attributed to the high concentrations detected in OMW.

Soils collected in the study area are characterized of slightly alkaline pH (7.2–8.2) and EC varying between 610 and 3,420 μS/cm. According to the Canadian thresholds for agricultural soils, shown in Table 4, EC is higher in samples collected from the walls of the disposal ponds in AC-1 and AC-2 sites.

Table 4
Selected parameters in waters and soils, as well as drinking water standards and Canadian thresholds for agricultural soils

	Waters (mg/L)	Drinking water standards [36–39] (mg/L)	Soils (mg/kg)	Canadian thresholds for agricultural soils [40] (mg/kg)
pH	6.5–8.9	6.5–8.5	7.2–8.2	6–8
EC (μS/cm)	92–2,480	~2,500 (20˚C)	610–3,420	2,000
Total hardness (mg $CaCO_3$/L)	130–431	Acceptable 80–100 mg/L, tolerable >200 mg/L but unacceptable >500 mg/L	–	–
Phenols	0–5	No health-based guideline value (suggested safe levels <0.5 μg/L [35])	5–142	3.8
NO_3^-	0–33	<45	–	–
SO_4^{2-}	5–71	≤250	–	–
PO_4^{3-}	0–1.8	No health-based guideline value (suggested safe levels <5 mg/L)	–	–
P_{avail}	–	–	1.5–289	–
Cl	4–47	<250	–	–
K	0.1–230	<12	187–4,842	–
Fe	<0.1	<0.2	7–233[a]	–
Cd	–	<0.005	0.2–0.8[a]	1.4
Cu	<0.1	<2	8–152[a]	63
Pb	–	<0.01	15–49[a]	70
Zn	<0.5	≤5	0.2–15[a]	200
Mn	<1.2	<0.05	1–181[a]	–
Ni	<0.1	<0.07	37–105[a]	50
Mo	0	<0.07	15–30[a]	5[b]
Cr	0.01–1.6	<0.05	18–80[a]	64

[a] Extractable fraction by diethylene triamine pentaacetic acid (DTPA).

[b] Canadian threshold indicates an interim remediation value.

Phenol concentration was very high in all sampling points and depths, exceeding in all cases the Canadian threshold value of 3.8 mg/kg for agricultural soils [40].

Surface soils in pond walls are very rich in available P (1.5–289 mg/kg). Soils show very high concentrations of Ni, Cu, and Mo, varying between 37–105, 8–152, and 15–30 mg/kg, respectively. These concentrations exceed substantially the Canadian thresholds for agricultural soils. Cr though exceeds locally threshold values. Concentrations of Cd, Pb, and Zn comply with Canadian threshold values. For Fe, K, and Mn showing high values in soils collected from ponds walls, no thresholds exist.

It should be mentioned, though, that results are affected from periodic OMW disposal on soil as well as from intense precipitation in the study area which resulted also in high level of pore water in drillholes 1 and 2.

4.2. Variography of soil and water samples

In order to ensure the proper calculation of the covariance function, which will be the main structural characteristic of the pollutants spatiotemporal distribution, it is necessary to work on a homogeneous RF. Detrending of the data-set, which is the statistical operation of removing trend from a series and is often applied to remove a feature thought to distort or obscure the relationships of interest, was done by the application of a Gaussian kernel on it [41]. The estimated mean trend in the case of phenol in water is shown in Fig. 3. The spatial trend is restored after each estimation process is completed.

The study of the histograms of the pollutant concentrations follows the subtraction of the trend by taking into account the mean concentration at each sampling location. Most calculated histograms are skewed (as for e.g. in Fig. 4(a) for water pH values). In order to assess data normality, a normal scores transformation [42] is applied to the detrended data. The resulting histogram for water pH values is shown in Fig. 4(b). Obviously, the transformed data follow the normal distribution.

The next step in the exploratory analysis is the investigation of the systematic dependencies in the data. A physically and statistically acceptable covariance model is sought to describe the correlation among data. Fig. 5 shows the average experimental covariance over all directions and the fitted spherical model for the case of phenol concentrations in water. The other pollutants also exhibit similar behavior. A spatial range of influence of 500–800 m appears according to model.

4.3. Assessment of risk for soil

A concentration map for phenols (mg/kg) in surface soil (sampling depth 0–25 cm) is shown in Fig. 6. AC-1 site is located at the lower left part of the figure while AC-2 site at the upper right part. Fig. 7 shows the concentration map for phenols in various soil depths (up to 150 cm) for the AC-1 disposal site.

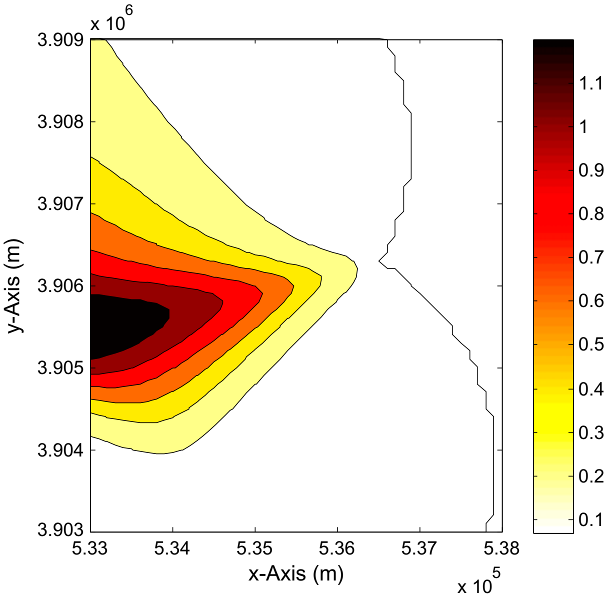

Fig. 3. Trend map for phenols (mg/L) in water.

As shown from Figs. 6 and 7, phenol concentration is very high in all surface sampling points exceeding in all cases the Canadian threshold value of 3.8 mg/kg for agricultural soils [40]. Hot spots indicating the highest concentration of phenols are shown in the upper soil layer (0–25 cm) in pond walls.

However, the concentration of phenols decreases with distance from ponds as well as with soil depth due to degradation of phenols on soil, also as a result of bacterial activity [43]. It is mentioned that the degradation of phenols in soils as well as their adsorption by clayey soils with a strong adsorption capacity minimizes the risk for groundwater contamination through leachate migration. This is beneficial in areas where accidental release of OMW from evaporation ponds is noticed or when OMW are used as source of irrigation. It is noticed though that this soil capacity is substantially reduced after continuous OMW applications on soil, thus increasing the risk for groundwater contamination.

Surface soils in pond walls are very rich in available P as shown in the concentration map in Fig. 8; however, P concentration decreases with distance form ponds and depth. Higher P concentration is shown in soil samples collected from the walls of the evaporation pond located in the AC-2 site (upper right part of Fig. 8). It is mentioned that at sites where no direct application of OMW on soils took place, the concentration of available P decreased with distance probably due to its precipitation in ponds.

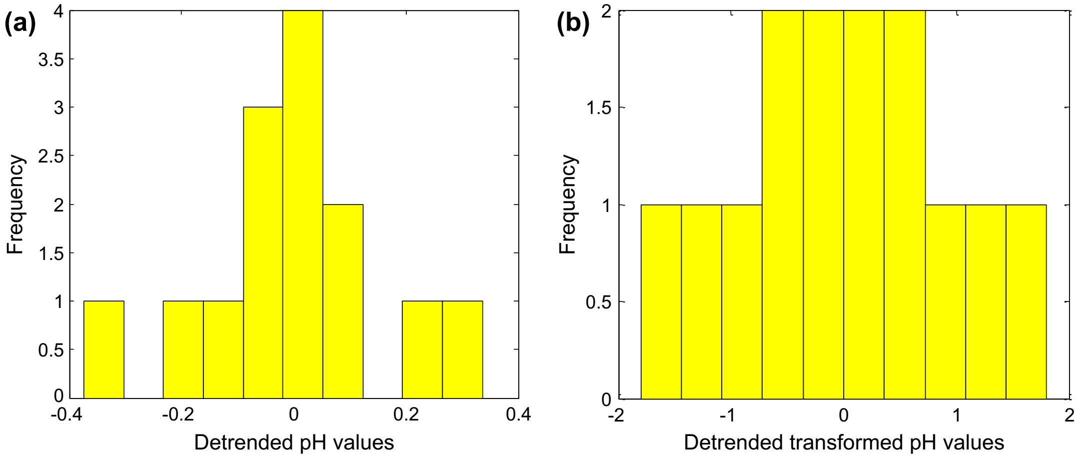

Fig. 4. Water pH values (a) before and (b) after normal scores transformation.

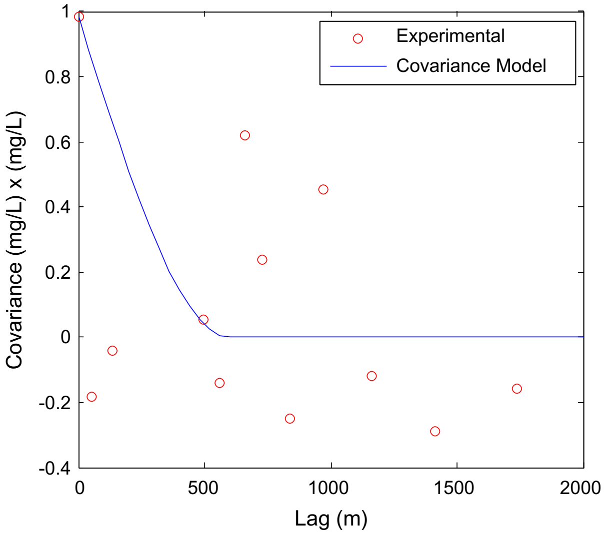

Fig. 5. Experimental and covariance model for phenols concentrations in water.

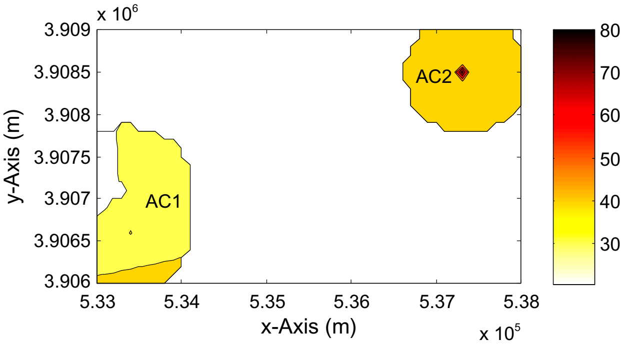

Fig. 6. Concentration map for phenols (mg/kg) in surface soil; threshold value is 3.8 mg/kg [40].

Overloading of soils with phosphate ions could result in P leaching, increased concentration of dissolved P in surface runoff, and thus increased risk for surface water contamination. A major environmental concern is associated with P accumulation in soil and the long period required, up to 20 years, so that P content reaches again acceptable levels for agronomic use [44]. High levels of P can be reduced only after 15–20 years of continuous crop harvesting, provided that no additional P from any source is added during this period [45].

As shown in Fig. 9, Ni concentrations are very high in all surface soils, reaching values between 70 and 100 mg/kg, that exceed the target value of 50 mg/kg [40] and may cause potential risk to ecosystems. Hot spots are clearly visible in large parts of AC-1 site due to direct disposal of OMW on soil. High Ni concentrations are also detected in some cases, in deeper soil horizons indicating potential risk for groundwater contamination. It may be also assumed that the presence of recalcitrant heavy metals in soils (namely, Ni, Cr, Mn, and Mo) could be the result of past olive oil milling activities when inferior steel quality equipment was used [46].

From the geostatistical risk analysis, it is deduced that risk for soils in OMW disposal and neighboring areas is rather high since phenols, available P and Ni exceed thresholds. If the entire study area is considered, risk is assessed as low to average. It has to be mentioned though that higher risk will be calculated if disposal of OMW takes place in other areas where soils are sandy, the content of clays in soils is limited, the disposal sites are close to the sea or other water resources, and the groundwater table is shallow.

Also, reliability maps showing the estimation error standard deviation were produced for the selected variables (Figs. 10–12). All maps display similar spatial behavior, since the estimation error depends on the geometric configuration of sampling points and the covariance model, both more or less equal for all elements. As expected, reliability is relatively low in sparsely sampled areas, an indication that more samples are necessary.

4.4. Assessment of risk for water

Fig. 13 shows a concentration map for phenols (mg/L) in water. High phenols concentration (average of 1.3 mg/L) was determined in water samples collected from one old well and two springs as well as in pore water sampled from two piezometers which are located close to the disposal ponds (in a distance of around 50 m). Hot spots are shown in the left central part of Fig. 13. For the water samples collected from other sampling points (streams, springs, and water supply pipes), phenols concentration varies around 0.1 mg/L (right part of Fig. 13).

Fig. 14 shows the map for Cr concentration in water (mg/L), ranging between 0.01 and 1.6 mg/L for samples collected from all water sampling points and piezometers. High concentrations are detected in water samples collected from one old well and two springs in 2012 (average of 0.58 and 0.37 mg/L, respectively). Hot spots are shown in the left central part of Fig. 14; high concentrations (ranging between 0.7 and 1.6 mg/L Cr) have been determined in pore water samples collected form piezometers installed in drillholes in a distance of around 50 m from the main evaporation pond in AC-1 site. The threshold value of 0.05 mg/L Cr for drinking water [36,39] is exceeded in these water samples.

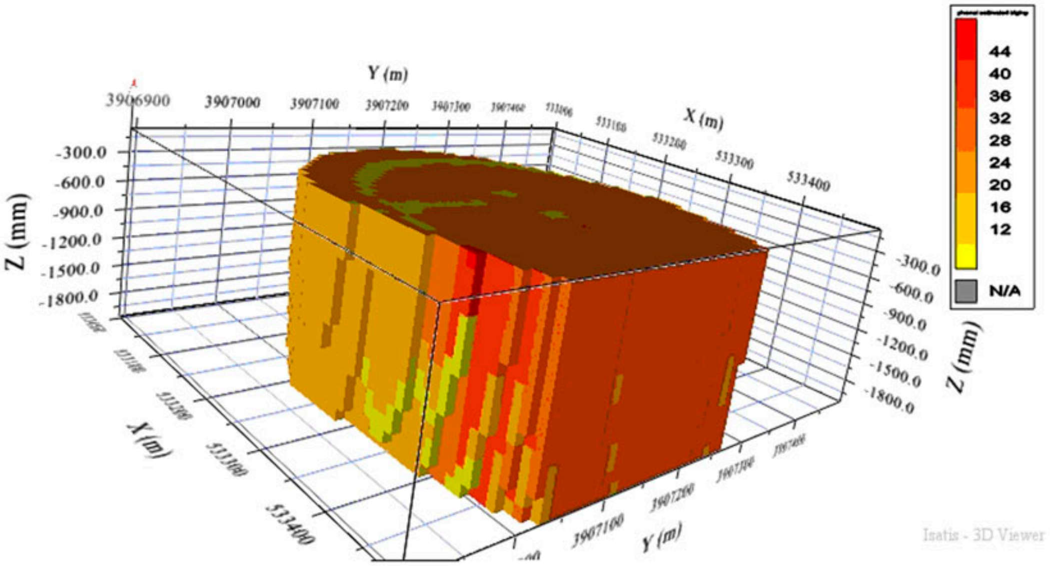

Fig. 7. Concentration map for phenols (mg/kg) in soil vs. depth (up to 150 cm); threshold value is 3.8 mg/kg [40].

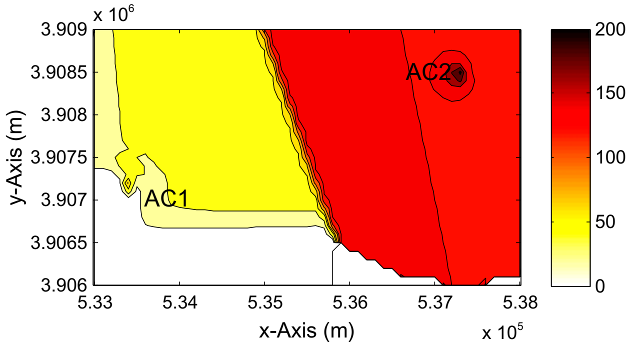

Fig. 8. Concentration map for P_{avail} (mg/kg) in surface soil; no threshold exists.

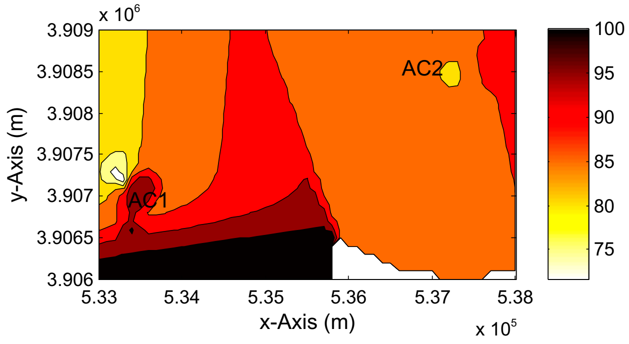

Fig. 9. Concentration map for Ni (mg/kg) in surface soil; threshold value is 50 mg/kg [40].

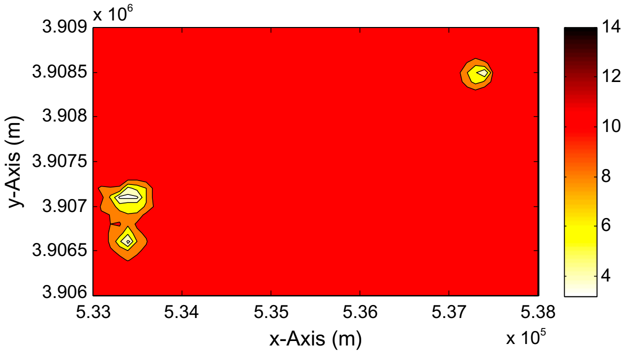

Fig. 10. Error map for Ni concentrations in surface soil (mg/kg).

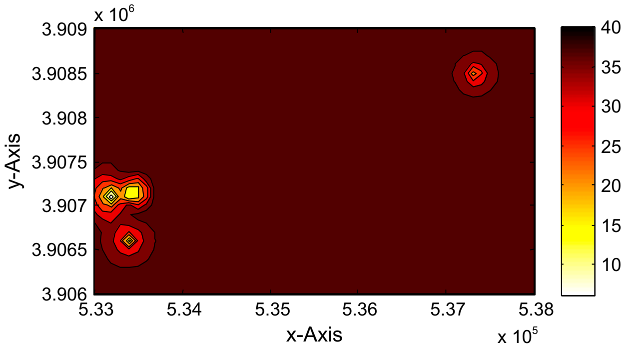

Fig. 11. Error map for P_{avail} concentrations in surface soil (mg/kg).

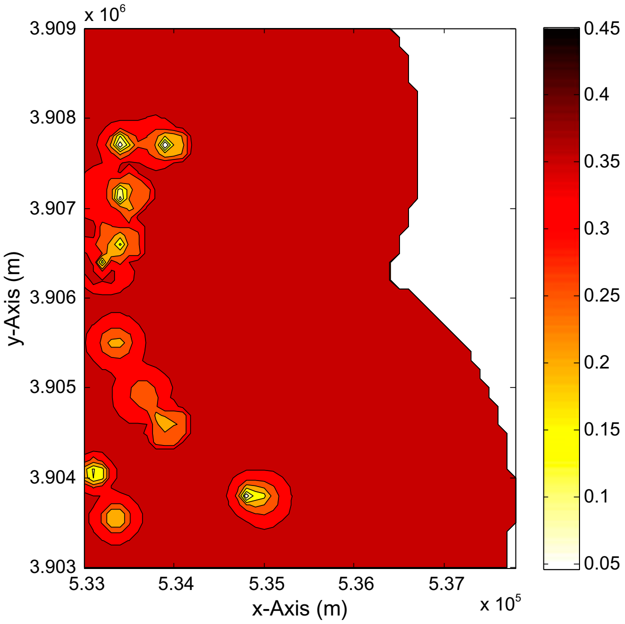

Fig. 12. Error map for phenol concentrations in water (mg/L).

Ni concentration shows similar behavior to Cr. A map for Ni concentration (mg/L) in water is shown in Fig. 15. Ni concentrations in the water samples collected from streams, springs, water supply pipes, and old wells are lower than 0.1 mg/L. The threshold value of 0.07 mg/L [38] for drinking water is exceeded only in water samples collected from two springs in the study area on May 2012 and October 2012. High Ni concentration, just below the threshold value of 0.07 mg/L, is seen occasionally for water samples collected from one old well. All these sampling points are located close to the AC-1 site in a distance of 700–2,250 m.

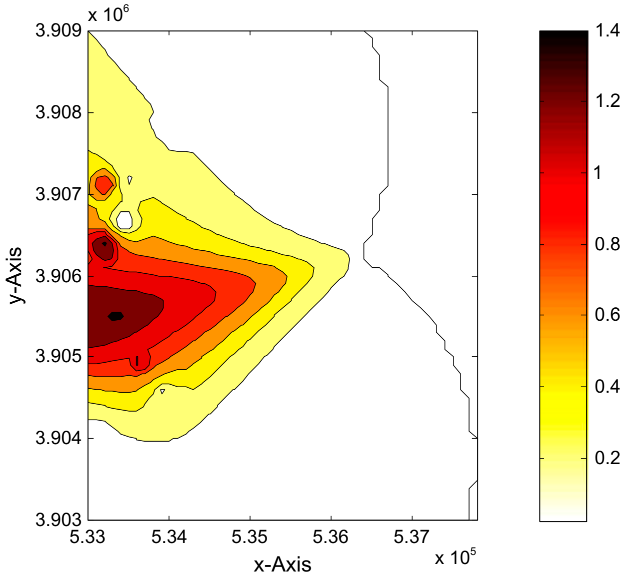

Fig. 13. Concentration map for phenols (mg/L) in water; no health-based guideline value, suggested safe levels <0.5 µg/L [35].

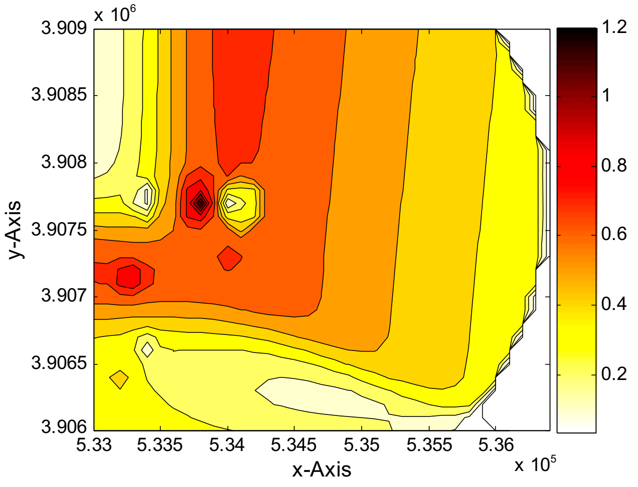

Fig. 14. Concentration map for Cr (mg/L) in water; threshold value is 0.05 mg/L [38].

The high risk associated to Ni is related to elevated concentrations recorded in soils (concentration map in Fig. 9). Part of Ni present in soils may be transferred due to disposal of acidic OMW and precipitation in deeper soil horizons and subsequently in groundwater.

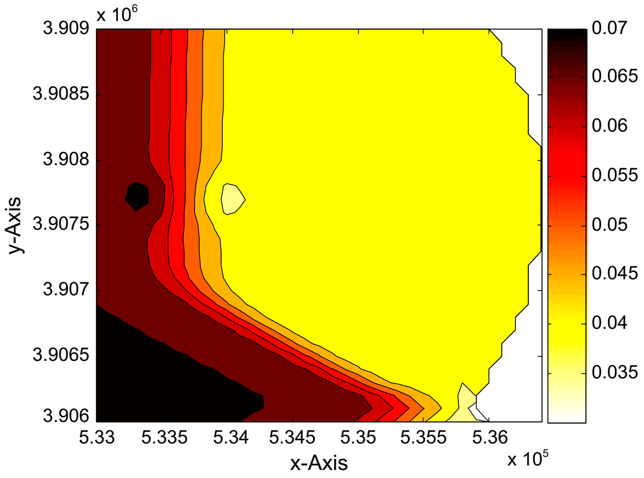

Fig. 15. Concentration map for Ni (mg/L) in water; threshold value is 0.07 mg/L [38].

4.5. Framework for monitoring soils and water bodies in areas affected by OMW disposal

In order to estimate the risk for soil and water in an area affected by OMW disposal, combined monitoring of soil and water quality needs to be carried out. If sufficient data are available, geostatistics may be used to produce concentration maps, identify hot spots, and assess the risk for all affected receptors.

The proposed approach for interested stakeholders proposes sampling and analysis of soils and waters over an appropriate time frame. Regarding water, existing streams, wells, and ponds may be sampled, since drilling for the installation of piezometers is usually expensive. In case no water sampling points are available, careful soil analysis as a result of frequent sampling would indicate the probability for potential contamination of surface and groundwater by considering the source of pollution, the polluting load, the frequency of disposal/discharge, the soil properties, and the depth of groundwater table.

Thus, a framework for the estimation of risk for groundwater based on soil analysis should briefly include:

(1) Profiles of concentrations of (organic or inorganic) contaminants in soil (if concentration drops substantially after a depth of 1–2 m, then risk for groundwater is expected to be low).
(2) Soil type (if soil has a high content of organic matter or high buffering capacity risk will also be low).
(3) Depth of groundwater table.
(4) Presence or not of an impermeable formation above the groundwater table (in this case practically no risk for groundwater is anticipated).

Additional sampling points and more frequent sampling should be considered if:

(1) The capacity of a mill for OMW production is much higher compared to that of the present study.
(2) More mills of the same capacity operate in the same area (AC-1 site in the present study is located at a distance of 4.2 km from the other active disposal site AC-2, thus no cumulative effects are anticipated).
(3) Soil is near saturation and groundwater table is shallow.
(4) The mill and the OMW disposal pond(s) are located in a coastal area where soil is sandy or intrusion of sea water is expected.

A point that needs to be underlined, in order to estimate risk for soils and especially groundwater in an area, is which thresholds for soils or soil use are considered and also which criteria are used to assess groundwater quality. It is known that in each country, different soil criteria are available (“action” for clean up or “no action” as in the Netherlands; according to the soil use “agricultural,” “residential,” or “industrial,” as in Canada, etc.; no soil thresholds exist for Greece).

For water, the most commonly used criteria are those for drinking water, although this may not be relevant in several cases (if, for example, groundwater is not used at all or is used only for irrigation; in this last case, if risk for humans needs to be assessed, the situation becomes very complex since bioavailable or phytoavailable fractions of contaminants, exposure routes, and duration, as well as a number of other parameters need to be assessed).

5. Conclusions

In the present study, the risk for soils and waters in an area of 15 km^2 due to the uncontrolled disposal of OMW has been estimated with the use of geostatistics.

Regarding soils, risk maps were produced for phenols, available P, and nickel. The analysis carried out indicates that several hot spots are present in the area under study, mainly in the vicinity of the evaporation ponds. Phenol and available P concentrations decrease with distance and depth, while higher Ni concentrations are noticed in higher soil depths. Thus, it is deduced that risk for soils in OMW disposal and neighboring areas is rather high. If the entire study area is considered, risk is assessed as low to average. The geostatistical analysis indicates that reliability of results is relatively low only in sparsely sampled areas.

Regarding waters, a couple of hot spots are identified regarding phenols, Ni, and Cr, mainly in areas located in the vicinity of OMW disposal sites. Regarding phenols, this is due to their adsorption on soils as well as their degradation as a result of bacterial activity. The low concentration of heavy metals in waters is due to their limited mobility in soils, the properties of soil, and the higher depth of groundwater table.

Finally, guidelines for the development of a framework aiming to assess soil and water quality and ultimate risk in similar areas are proposed.

Acknowledgments

The authors from Technical University of Crete and Hellenic Agricultural Organization DEMETER would like to acknowledge the financial support of the European Commission in the framework of the LIFE07 ENV/GR/000280 project entitled "Strategies to improve and protect soil quality from the disposal of olive oil mills wastes in the Mediterranean (PROSODOL)".

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