Environmental Engineering and Management Journal *June 2019, Vol. 18, No. 6, 1297-1309*
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

OPTIMIZATION OF HEAVY POLLUTED SOIL FROM OLIVE MILL WASTE THROUGH THE IMPLEMENTATION OF ZEOLITES

Maria K. Doula[1], Antonis A. Zorpas[2]*, Vassilis J. Inglezakis[3],
Jose Pedreno Navvaro[4], Dimitrios J. Bilalis[5]

[1]Benaki Phytopathological Insitute, 8 Stef. Delta, 14561 Kifissia, Greece
[2]Cyprus Open University, Faculty of Pure and Applied Sciences, Environmental Conservation and Management,
Laboratory of Chemical Engineering and Engineering Sustainability, P.O.Box 12794, 2252, Latsia, Nicosia, Cyprus
[3]Nazarbayev University, School of Engineering, Chemical Engineering Department,
53 Kabanbay batyr ave., Astana, Republic of Kazakhstan
[4]Department of Agrochemistry and Environment, Miguel Hernández University of Elche,
Avda. de la Universidad s/n, 03202 Elche, Alicante, Spain
[5]Agricultural University of Athens, Department of Crop Science, Lab of Agronomy, Iera odos 75, Athens, 11855, Greece

Abstract

Clinoptilolite (Clin), the most widely used natural zeolite in environmental applications, was used as soil additive to investigate its effectiveness in protecting and improving the quality of soils that received surface disposal of OMW, as well as in limiting nutrients leaching from the degraded soils. Clin was added in a batch experiment of 18 months, where OMW were added in evaporation ponds and on soil for a period of more than 12 years. The zeolite was added as dust (particle diameter < 0.8 mm) and granules (particle diameter range from 0.8 - 2.5 mm). Several soil parameters such as pH, electrical conductivity, organic matter, polyphenols, N, P, K, Na, Ca, Mg, Cu, Mn, Zn and Fe were controlled bimonthly. The addition of Clin in a soil that received OMW for 12 decreased excess leaching of K, Fe, Mn and Cu in accepted level. The total organic matter and nitrogen contents of soil were controlled at almost constant values ($p<0.05$) in contrast with polyphenols that were not significantly ($p<0.05$) decreased after the addition of zeolite. Na leaching from Clin was measured and found to be high, but only during the first two months after Clin addition on soil. Therefore, Clin could be an effective soil additive for areas where OMW surface disposal degrades soil quality.

Key words: bio-solid management, clinoptilolite, olive mill wastes, soil additive, soil degradation, soil rehabilitation, soil remediation

Received: August, 2018; Revised final: January, 2018; Accepted: March, 2018; Published in final edited form: June 2019

1. Introduction

It is well known that soils, which receive Olive Mill Wastes (OMW), are eventually becoming overloaded with organic matter of unknown and insufficient quality as well as inorganic nutrients and polyphenols. Clinoptilolite (Clin), the most widely used natural zeolite in environmental applications, was used as soil additive to investigate its effectiveness in protecting and improving the quality of soils that received surface disposal of OMW, as well as in limiting nutrients leaching from the degraded soils. Olive oil production is considered to be one of the oldest agricultural processing particularly in the Mediterranean (Zorpas and Costa, 2010) and typically produced (Vlyssides et al., 2000; Zorpas and Tzia, 2008) with the following extraction processes: (a) using a traditional discontinuous press process (Dias et al., 2004), (b) using a two phase and (c) using a three-phase centrifugal extraction

---

[*] Author to whom all correspondence should be addressed: e-mail: antonis.zorpas@ouc.ac.cy; antoniszorpas@yahoo.com; Phone: +357 22411936, Fax: +357 22411601

technique (Vlyssides et al., 1999). Through the production process, several wastes and by-products are created such as olive wood and leaves, cake, kernel, and olive mill wastewater (Peri and Proietti, 2014). This waste (OMW) present composition which mainly depends on many factors such as climatic conditions, local and seasonal nature of oil production, soil properties, cultivation practices, etc. (Inglezakis et al., 2012; Mohawesh et al., 2014).

The main problem is attributed to its toxicity due to the presence of phenolic compounds, its high organic load (nitrogenous compounds, proteins, sugars), its dark color and offensive odour. Is estimated that annually more than 2.1 x 10^6 t of olive oil (Gohary-El et al., 2009; Goula and Lazarides, 2015; Zorpas and Costa, 2010) are produced worldwide. Every 1 t of olives produces more or less 1.2-1.8 m^3 t^{-1} OMW, while the yearly total amount in the Mediterranean area is more than 30 x 10^6 m^3 y^{-1} (Gohary et al., 2009; Zorpas and Costa, 2010) with Greece, Italy and Spain to be the main producers (Pavlidou et al., 2014). OMW is an aqueous, dark, foul-smelling and turbid liquid, which includes emulsified grease, is easily fermentable, has high organic load (40-165 g L^{-1}), low pH (4.5 - 6.0), high electrical conductivity (3.5 - 12.5 dS m^{-1}) and high polyphenols concentration (3.0 - 24 g L^{-1}).; while at the same time is also rich in nitrogen and phosphorus and contains trace metals (Fe, Cr, Pb, Cu, Ni, Cd, Zn, Mn) (Goula and Lazarides, 2015; Kavvadias et al., 2010; Pavlidou et al., 2014; Zorpas and Costa, 2010).

As there are no any specific European legislations or directives focuses on the management of OMW, each country issues its own national or regional regulations (Zorpas and Costa, 2010). In the Mediterranean region, where for the last year's subtropical climates are presented, untreated OMWs are often discharged directly into sewer systems and water streams or disposed in evaporation ponds/lagoons and on soils despite the fact that such management options are not allowed in most of the Mediterranean countries. Uncontrolled disposal of OMW causes significant environmental pollution (Goula and Lazarides, 2015; Pavlidou et al., 2014; Zorpas and Costa, 2010) with unforeseeable effects on the quality of soil and of surface and ground water systems (Karaouzas et al., 2011).

Soil properties are strongly affected by the direct disposal of OMW on soil as well as, in unprotected evaporation ponds. Soils loaded with OMW are rich in organic matter, inorganic nutrients and polyphenols (Kavvadias et al., 2010). Although organic matter and nutrients could be beneficial for soil fertility and necessary for plant growth, serious soil degradation is probable due to very high concentrations of both inorganic and organic constituents and especially polyphenols. Moreover, the long-term implementation of untreated OMW decreases the saturated hydraulic conductivity, increases soil's disposition to water repellency (Mahmoud et al., 2010) and seems to slow down the mobility and consequently the activity of pesticides (Mahmoud et al., 2010). Furthermore, the addition of the insufficiently stable organic matter of wastes, although it leads to a general increase in soil organic matter, it may result in a number of negative effects on soil properties and plant growth, such as increase in mineralization rate of native organic carbon, induction of anaerobic conditions and release of phytotoxic substances (Cereti et al., 2004; Kavvadias et al., 2010; Komilis et al., 2005). Natural zeolites have been the subject of investigation by many researchers, who implement them in heavy metals adsorption, water purification and softening, soil remediation etc. (Costa et al., 2012; Doula, 2006; Szollosi-Mota et al., 2017; Zorpas et al., 2009; Zorpas, 2012 and 2015). However, there are limited data to support long-term use of natural zeolites in real soil remediation (Doula, 2007; Doula et al., 2012).

This paper aims to investigate and examine whether the natural zeolite, namely Clinoptilolite (Clin), could be used as soil additive in OMW disposal areas and more specifically, whether Clin could limit excess leaching of OMWs' constituents (i.e. K, P, Fe, Mn, Cu and others); stabilize the uncontrolled addition of soil organic matter and nitrogen; and reduce soil polyphenols' concentration.

2. Material and methods

2.1. Clinoptilolite

According to Clin (which produced from Pentalofos, Thrace in Northern part of Greece) chemical composition (APHA, 1985), it is a Ca-rich zeolite with almost no Fe content ($Na_{0.2}K_{0.6}Mg_{0.7}Ca_{2.0}Al_{6.2}Si_{29.8}O_{72}$ x $19.6H_2O$), while the Si/Al ratio is equal to 4.8 indicating that the zeolite belongs to the heulandite group of natural zeolites and is Clinoptilolite. The Cation Exchange Capacity (CEC) of Clin, with respect to its formula is 2.35 meq g^{-1}. The analysis through XRD spectrum (Fig. 1) indicated that clinoptilolite, montmorillonite, illite, cristobalite and albite are present in the mineral, whereas the Clin content is approximately 70% (the properties of Clin are presented in Table 1).

2.2. Pilot area

The pilot area (Fig. 2) is located in the Municipality of Rethymnon, Crete; North latitude is 35◦17′, while the East longitude is 24◦21′. The region has subtropical Mediterranean climate and is characterized by mild winters and dry-hot summers. Soils of the area are clayey or silty clayey, slightly to moderately alkaline and rich in carbonates (Kavvadias et al., 2010). The selected disposal area (1 ha = 10000 m^2) with almost 5% slope, includes two evaporation ponds constructed after soil excavation and without using any waterproof membranes/geotextiles or other protective media to avoid waste leaching to higher soil depths and towards underground water. The area was used for OMW disposal for more than 12 years.

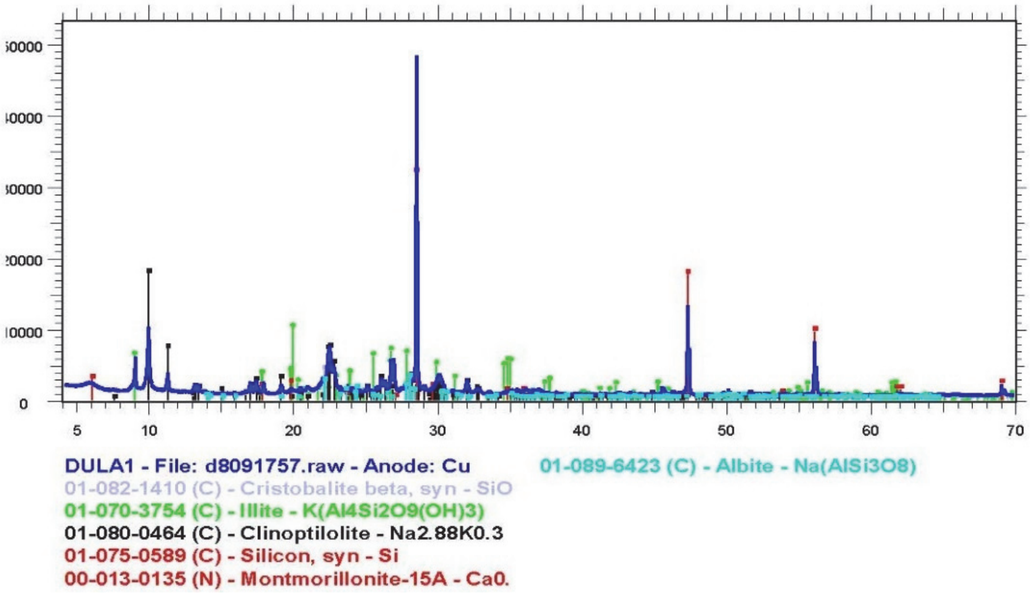


Fig. 1. XRD pattern for Clinoptilolite used for the experiments

Table 1. Main properties of the clinoptilolite used for the experiments

Parameter	***Content/value***
% Clinoptilolite	69
% Cristobalite	5.1
% Illite	7.0
% Montmorillonite	15
% Albite	3.0
% Amorphous	-
BET Specific surface area (SSA), $m^2\ g^{-1}$	31.0
Monolayer value, $cm^3\ g^{-1}$	7.12
Specific porous volume, $cm^3\ g^{-1}$	6.2×10^{-2}
Pore diameter, (Å)	< 20
Specific value of adsorbed N_2 $cm^3\ g^{-1}$	54.6

Significant difference at p<0.05

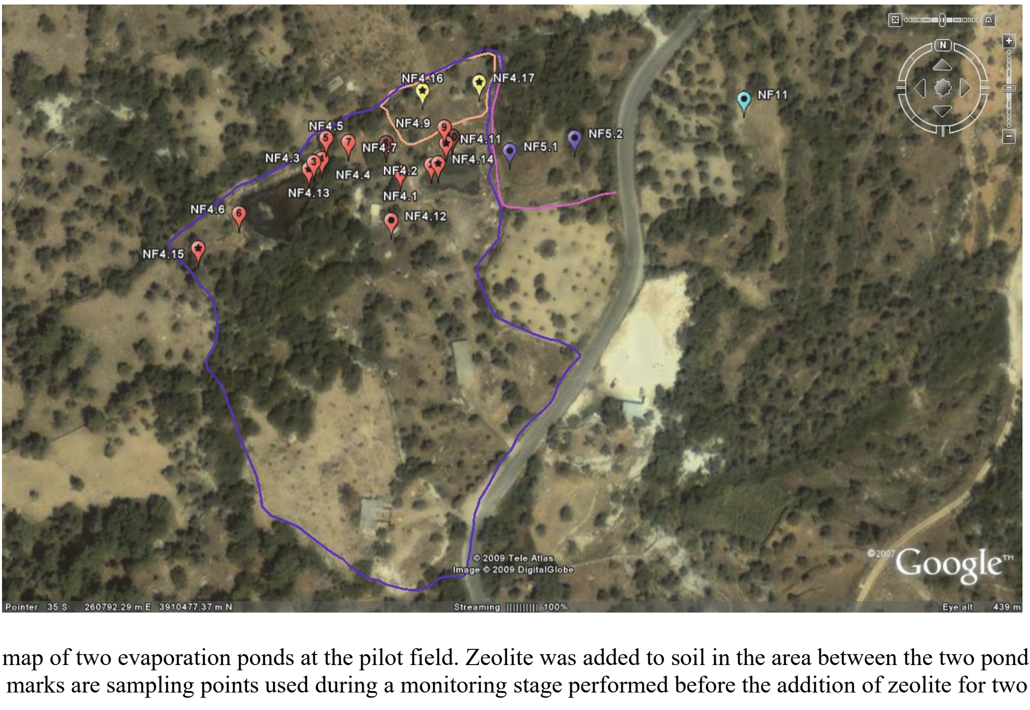


Fig. 2. The map of two evaporation ponds at the pilot field. Zeolite was added to soil in the area between the two ponds. Red and yellow marks are sampling points used during a monitoring stage performed before the addition of zeolite for two years

In general, waste is disposed in the two evaporation ponds without any pretreatment, as for example, separation of solid waste from wastewater, while usually, due to large oil production, waste overflows and affects the surrounding soils. Three plots of 8.5 m x 12 m in the vicinity of the evaporation ponds that accept OMW due to overflowing (Fig. 3) were used for the pilot experiments using the same treatment. In November 2013, each plot was divided into four sub-plots (Fig. 3) and the zeolite was added as dust (particles diameter < 0.8 mm) and in granules (particle diameter of 0.9 - 2.5 mm).

Clin was incorporated in the soil by tilling the plots until 25 cm depth. In order to investigate the effects of Clin addition for each plot and to compare them with current situation of the soils in the vicinity of the ponds, a control plot was also constructed; control plot accepts OMW waste but no Clin was added.

2.3. Chemical parameters of the OMW

OMW samples, which were produced from a three-phase mill, were collected regularly during the experiment implementation and their main chemical parameters were determined by using standard methods of analysis (APHA, 1985; Zorpas and Costa, 2010).

2. 4. Soil samples collection and analyses

The pilot area was monitored for 18 months by collecting soil surface soil samples (0 – 25 cm) from the 12 sub-plots bimonthly. For each plot, a homogenized sample (of 5 kg) was prepared by collecting and mixing three sub-samples collected from different locations of plots. Several soil parameters (pH, EC, Organic Matter, total Kjeldahl-N, P, K, Ca, Na, Mg, Mn, Fe, Cu, Zn, polyphenols) were determined by using standard methods of analysis (Box, 1983; APHA, 1985; ISO-11465, 1993; ISO-11260, 1994; ISO-11261, 1995; ISO-14235, 1998; ISO-14870, 2001; Zorpas and Costa, 2010). Statistical analysis was performed using SPSS v.2.0.

3. Result and discussions

Table 2 presents the characterization of the OMW disposed in the pilot area as collected during the experimental period. BOD varied from 35-42 g L^{-1}, while COD from 55-74 g L^{-1}. Polyphenols were in the range of 8.5-9.2 g L^{-1} with the total nitrogen to be in the range of 751-790 g L^{-1} and the total organic carbon between 34.1-37.5. pH was low and less than 5.5. Table 3 presents the main parameters of the soil samples collected from (a) the pilot plots before the addition of zeolite (referred as degraded soil) and (b) the wider area; i.e sites outside the disposal area which have never accepted OMW disposal and thus are considered unaffected (referred as clean soil).

Fig. 4a-e present's soil organic matter (SOM) content of the pilot plots shows that, despite the surface wastes disposal events in March and May 2014, the measured SOM values did not present significant variation. On the contrary, for the control sub-plots the variation of SOM follows the waste disposal events (January until May is the period of disposal). No significant difference between the four treatments was observed; indicating that particle size and amount added has no any significant effect

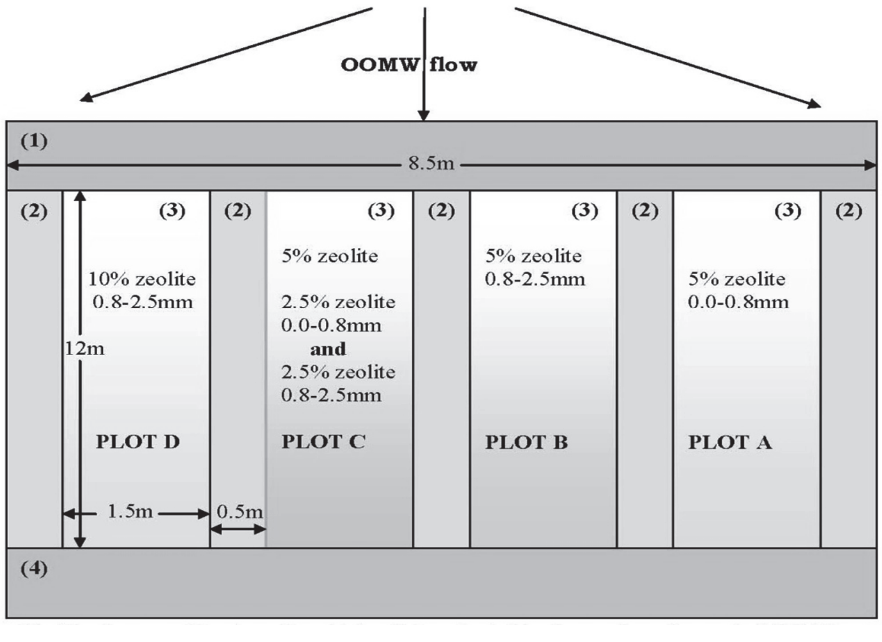


Fig. 3. Experimental plots and description of the applied experimental strategy for the application of Clin: (1) Control plot without zeolite which is affected by the surface disposal of OMW; (2) Buffer zone between the experimental plots; (3) Experimental plots with different zeolite content; (4) Blank zone to separate the pilot plots from the wider field

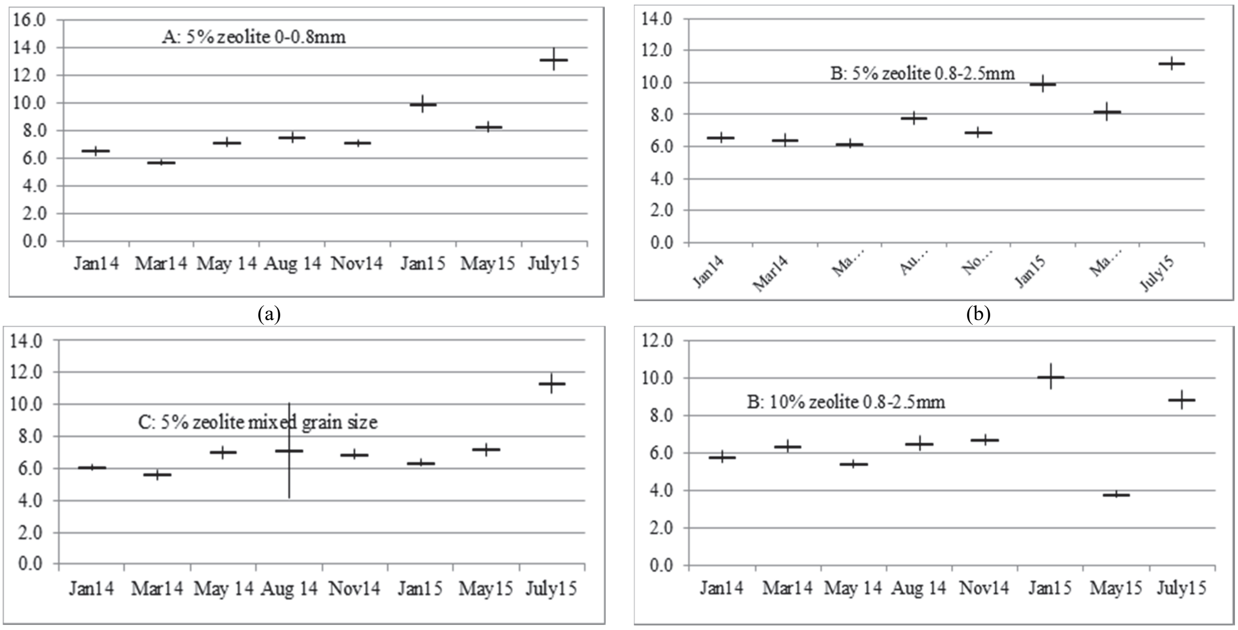
Table 2. Chemical parameters of the OMW disposed at the pilot area

Parameter	***Values***	***Average***	***Standard Deviation***
pH	4.9 – 5.4	5.1	1.6
Electrical Conductivity, dS cm^{-1}	7.6 – 8.1	7.75	1.1
Total Organic Carbon, g L^{-1}	34.1 – 37.5	36.9	4.5
BOD, g L^{-1}	35.1 – 42.6	40.6	6.3
COD, g L^{-1}	55.2 – 74.9	69.3	16.9
Total N, mg L^{-1}	750.6 – 790.4	776.1	48.4
Total polyphenols, g L^{-1}	8.5 - 9.2	8.8	0.9
Mg, mg L^{-1}	152.1 – 170.0	157.9	23.9
K, g L^{-1}	4.21 - 4.75	4.55	0.74
Ca, mg L^{-1}	430.1 – 500.6	477.7	125.6
Na, mg L^{-1}	106.9 – 118.0	111.8	12.4
P, mg L^{-1}	430.6 – 480.7	459.1	47.6
Cl^-, mg L^{-1}	89.4 – 118.2	92.3	11.8
S, mg L^{-1}	180.4 – 210.9	199.4	31.9
B, mg L^{-1}	5.10 - 5.49	5.22	0.56
Cu, mg L^{-1}	31.52 – 36.73	33.21	6.60
Fe, mg L^{-1}	240.1 – 265.7	255.9	19.8
Mn, mg L^{-1}	11.74 – 12.10	11.87	1.12
Zn, mg L^{-1}	19.0 – 22.3	21.2	2.6

Table 3. Critical levels of some main soil properties and their values as measured for the degraded soil samples collected from the OMW disposal area (i.e. degraded soil) and from a "clean area" that is not affected by the OMW disposal (i.e. clean soil)

Soil properties	***Normal average range***	***High Rich***	***Very high***	***Excessive***	***Degraded soil***	***Clean soil***
pH	6-8				6.7	7.7
EC, mS/cm	2.00			>4.00	4.5	0.6
Organic matter, %	> 3.4	> 5			29	4.3
Total Kjeldahl N, %		> 0.3			11	31
Available P-Olsen, mg kg^{-1}	12-28	>33-36	40-50		450	10
Exchangeable Mg cmol kg^{-1}	1.20-2.20		> 2.20		11	2.0
Exchangeable K cmol kg^{-1}	0.26-0.60		>1.2	>2.0	7.0	0.95
Exchangeable Ca cmol kg^{-1}	2.5-3.8		> 20		77	27
Available Cu (DTPA extractable) mg kg^{-1}		> 3		>20	4.6	1.4
Available Fe (DTPA extractable) mg kg^{-1}			> 50	> 100	127	13
Available Mn (DTPA extractable) mg kg^{-1}			> 50		33	12
Available Zn (DTPA extractable) mg kg^{-1}			> 8.1		7.6	0.72
Polyphenols mg kg^{-1}	target value: 0.05 / intervention value 40				101	21

Significant difference at p<0.05

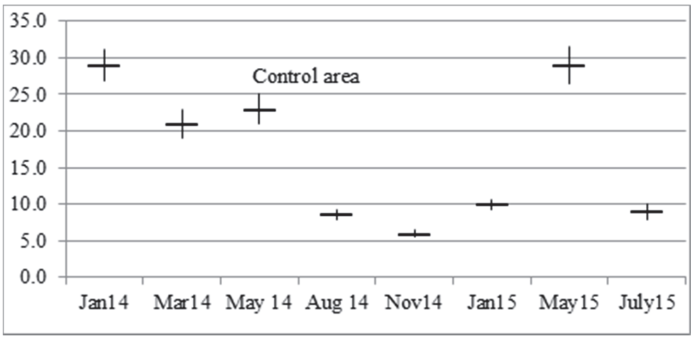


(a)

(b)

(c)

(d)



(e)

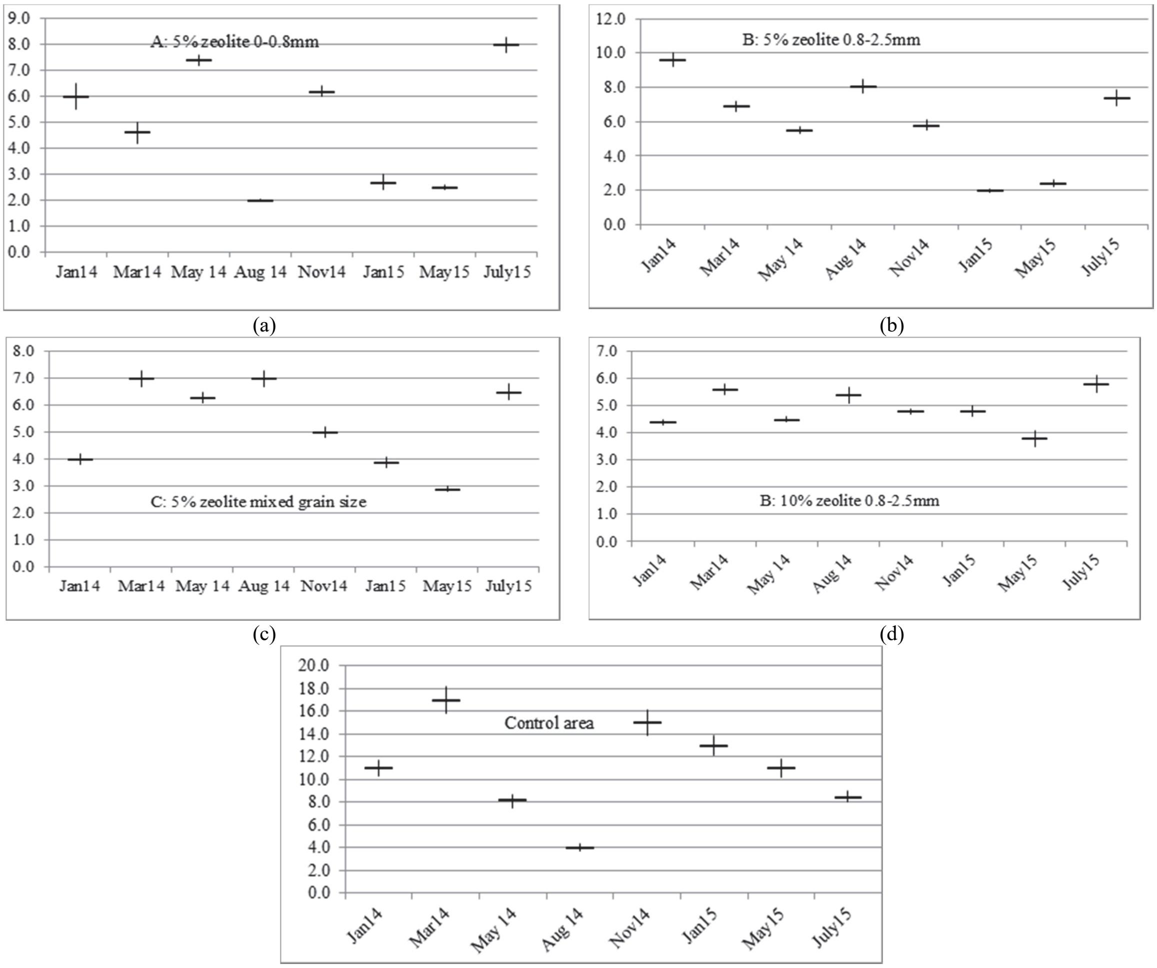
Fig. 4. (a) Organic matter (%) collected from the pilot zeolite area with 5% ainezeolite, 0-0.8mm; (b) Organic matter (%) collected from the pilot zeolite area with 5% zeolite, 0.8-2.5 mm; (c) Organic matter (%) collected from the pilot zeolite area with 5% zeolite mixed grain size; (d) Organic matter (%) collected from the pilot zeolite area with 10% zeolite, 0.8-2.5mm; (e) Organic matter (%) from control area

. As Fig. 4a-e demonstrates, the values of SOM at the control plots are extremely high compared to the limit of 5.0%, (Table 3 due to surface disposal of raw OMWs. Apart from the OMWs disposal, the accumulation of SOM is also enhanced by the high clay content of the soil (Jarboui et al., 2008). Fig. 3 also indicates that the addition of Clin has a dual effect; decreases and in the same time stabilizes the SOM content. This dual effect is significant as these lower SOM values are still rendering the soil as “rich” while stabilization enhances soil properties.

In particular, is well known that the accumulation of insufficiently stable SOM may cause various negative effects on soil properties including generation of anaerobic conditions and release of phytotoxic substances (Cereti et al., 2004). This probably happens due to the improvement of bulking density of the soil because of the presents of zeolite (Zorpas et al., 2008) aeration and thus to the enhancement of soil microorganisms’ activity to biodegrade SOM. The activity of the bacteria to biodegrade SOM is enhanced by Clin due to acceleration of mass transfer rate of water, oxygen, nutrients and hydrocarbons and also due to the improvement of water content of the soil which, in turn, results in improved hydrocarbon/water interface for bacterial growth and metabolism (Liang et al., 2009). Total nitrogen content (Fig. 5a-e) was also significantly lower in pilot plots than in control plots. Moreover, it is observed that samples collected from plots D (10% zeolite of 0.8 - 2.5 mm grain size) had lower and more stable values during the experimental period. Since most of the nitrogen content in soils is in organic form, the enhanced decomposition of the organic molecules due to Clin addition will also affect N concentration, which found to follow the same trend as SOM. Thus, as far as SOM and total nitrogen contents are concerned, the soil of the pilot plots can be characterized as rich and as containing stable values of SOM and nitrogen and therefore, the addition of zeolite improved both soil properties. The specific area of soil which for 12 years received OMW suffer from persistent high salt concentrations as previous studies have shown (Kavvadias et al., 2010).

EC is considered to be very high (up to 6.0 mS cm^{-1}) even though after 12 years of disposal. The implementation of Clin on the degraded soils seems to have positive result since soil salinity is a major degradation and abiotic factor limiting crop production (Zorpas et al., 2009). Al-Busaidi et al. (2008) used 5% Ca-rich clinoptilolite as soil amendment and found that the zeolite application could effectively improve salinity stress, nutrient balance in soil, and enhance water and salt holding capacity. The addition of zeolite was found to affect soil EC (Fig. 4a). A decrease in EC was recorded during the first three samplings; however, EC was increased again during the next samplings, mainly due to the OMW disposal in March and May 2014. Despite this increase, plots D (10% zeolite of 0.8 - 2.5 mm) and plots C (5% zeolite of mixed grain), had the lowest and most stable EC values compared to the A, B and to the control plots. Regarding the available phosphorous content (Table 4), although a slight decrease in its concentration was detected for plots C and D, it seems that zeolite is not capable to reduce and control the excess amounts of phosphorus added on soil with the disposal of OMW. Also, no significant effect of zeolite addition on polyphenols content was detected for plots A and B (Fig. 6b), while decrease in polyphenols concentration and relative stabilization was recorded for plots C and D, in agreement with the results obtained for the reduction and stabilization of SOM (Fig. 6a).

Apart from high soil EC, soils at OMW disposal areas have very high exchangeable K concentration as previous studies have shown (Kavvadias et al., 2010). Clin retained large amounts of K during the experiment (Fig. 6c); K ions were retained and held at zeolite’s active sites, inside and/or outside its framework. Thus, the increase in K concentration as seen in Fig. 6c is not attributed to the retention of K^{+} by soil particles but it is due to the retention by the zeolite. This, in turn, inhibits extent K leaching from soil and favors slow release of the cation, contributing thus to the improvement of soil quality and to the prevention of nearby systems overloading.



(a) (b)

(c) (d)

(e)

Fig. 5. (a) Total nitrogen of soil samples (mg g^{-1}) collected from the pilot zeolite area with 5% zeolite 0-0.8mm, (b) Total nitrogen of soil samples (mg g^{-1}) collected from the pilot zeolite area with 5% zeolite 0.8-2.5mm, (c) Total nitrogen of soil samples (mg g^{-1}) collected from the pilot zeolite area with 5% zeolite mixed grain size, (d) Total nitrogen of soil samples (mg g^{-1}) collected from the pilot zeolite area with 10% zeolite 0.8-2.5mm, (e) Total nitrogen of soil samples (mg g^{-1}) collected from the control area

In plots A (5% Clin of 0.8 - 2.5 mm) zeolite succeeded to stabilize the concentration of K, however for the other plots, K concentration values were higher but not stable. The final results are considered to be very interesting, considering that the disposal of OMW causes a substantial increase in soil K concentration which in almost all cases exceeds the threshold of 2.0 cmol kg^{-1} (Table 3). Kavvadias et al., (2010) state that the potential for accumulation of K in soil due to OMW disposal is high and can adversely alter soil properties. Moreover, since excessive concentrations of the element can also be found in deeper soil layers, the uncontrolled disposal of raw OMW in evaporation ponds or directly on soil, may cause K leaching to the groundwater. Potassium present in soil solutions is vulnerable to loss through leaching, particularly in soils with limited K fixing capacity (i.e. have low content of hydrous micas and illite clays) as well as in areas where large quantities of K^+ are introduced (e.g. disposal of wastes rich in K, fertilizers). Arienzoa et al. (2009) underlined that increased exchangeable K levels affect soil hydraulic conductivity and infiltration rates negatively.

For all these reasons, it is important to control the very high K concentrations in soils that accept OMW and it seems that Clin has the ability to improve this soil property. However, Clin did not succeed to control the concentration of exchangeable Mg and Ca (Table 4). Mg and Ca were decreased in soil meaning that, their concentrations were increased in soil leachates. This behavior is partly owed to the very high K retention by the zeolite through an ion exchange process. Due to the very high soil K concentration, K ions from soil solution force Ca and Mg ions from the zeolite framework to leave their sites and enter to soil solution (Doula et al., 2012).

The reduction of soil Ca affected directly the $CaCO_3$ content, which was found to decrease in all four plots soils (the higher decrease was recorded for plots A, 5% Clin of 0.8 - 2.5 mm). However, despite the decrease in $CaCO_3$ content, which is pH determined factor in soils, the soil pH was not reduced (Table 4); on the contrary pH was increased in all plots due to the buffering capacity of Clin, indicating protection of soil against the acidity of OMW and $CaCO_3$ reduction.

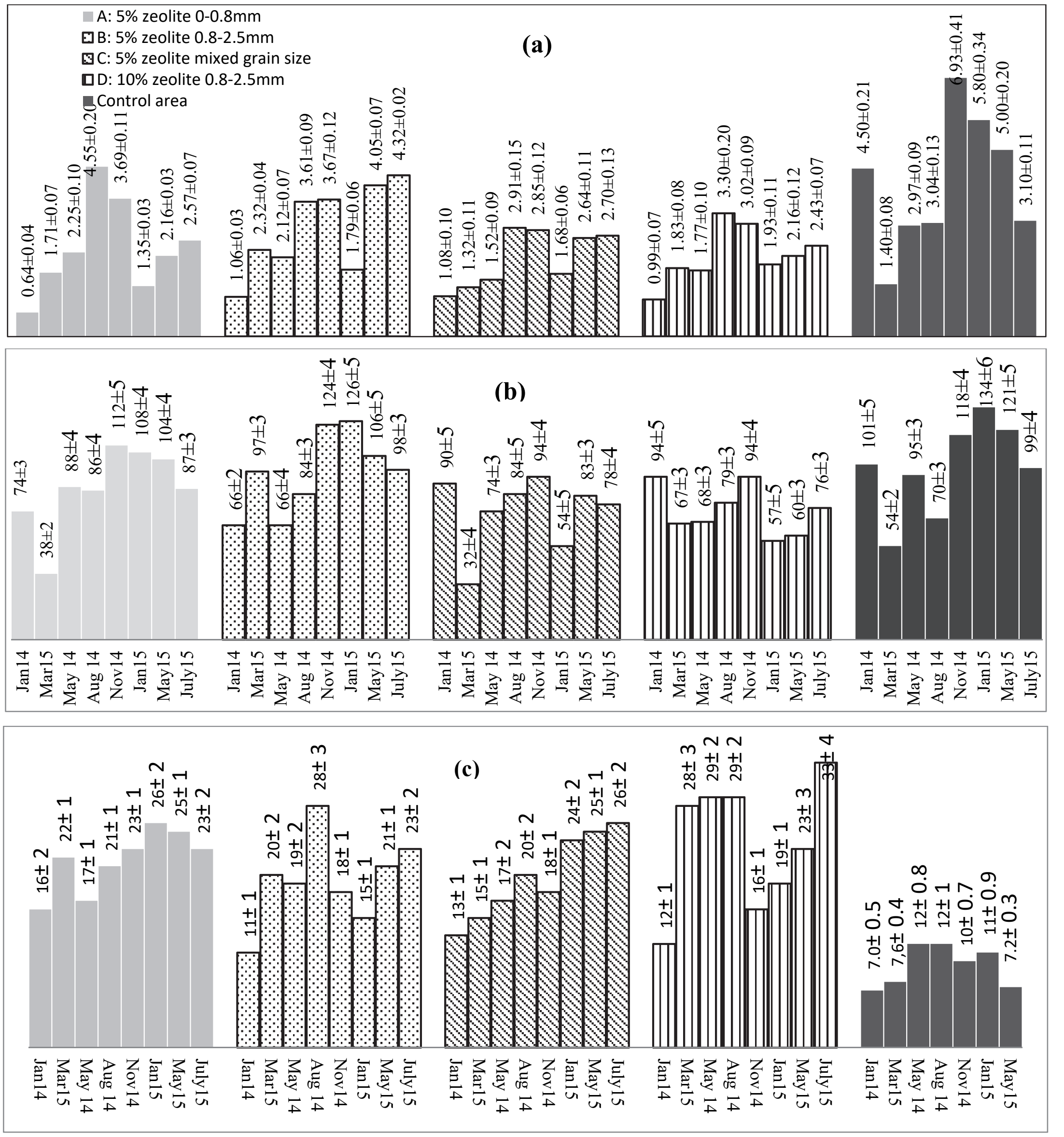


Fig. 6. (a) Electrical conductivity (mS cm^{-1}); (b) polyphenols (mg kg^{-1}); and (c) exchangeable K (cmol kg^{-1}) of soil samples collected from the pilot zeolite area in relation to zeolite ratios and sampling dates

Available Fe (Fig. 7a), Mn (Fig. 7b) and Cu (Fig. 7c) were increased in soil after Clin addition and followed the same behavior as potassium. Kavvadias et al. (2010) indicated that, between Fe, Cu, Mn and K, Fe and Cu are the two with the highest risk for soils that accept OMW, considering that (i) iron toxicity corresponds to Fe levels > 100 mg kg^{-1} (ii) Cu levels > 3.0 mg kg^{-1} are characterized as high and that (iii) the majority of soils at OMW disposal areas have higher values than the thresholds for both metals (Table 3).

Clin succeeded to retain high concentrations of Fe and Cu, which it is anticipated to be released slowly to soil solution. The results for these three metals were satisfactory for all plots without high variability among the different treatments. However, it seems that zeolite failed to increase Zn (Fig. 7d) and thus, leaching of Zn is likely to occur. Moreover, plots A seem to maintain significant values of Zn, which could be comparable to the values of the control plots. However, Clin did not succeed to control the concentration of exchangeable Mg and Ca (Table 4). Mg and Ca were decreased in soil meaning that, their concentrations were increased in soil leachates. This behavior is partly owed to the very high K retention by the zeolite through an ion exchange process. Due to the very high soil K concentration, K ions from soil solution force Ca and Mg ions from the zeolite framework to leave their sites and enter to soil solution (Doula et al., 2012). The reduction of soil Ca affected directly the $CaCO_3$ content, which was found to decrease in all four plots soils (the higher decrease was recorded for plots A, 5% Clin of 0.8 - 2.5 mm). However, despite the decrease in $CaCO_3$ content, which is pH determined factor in soils, the soil pH was not reduced (Table 4); on the contrary pH was increased in all plots due to the buffering capacity of Clin, indicating protection of soil against the acidity of

OMW and $CaCO_3$ reduction. Available Fe (Fig. 7a), Mn (Fig. 7b) and Cu (Fig. 7c) were increased in soil after Clin addition and followed the same behavior as potassium. Kavvadias et al. (2010) indicated that, between Fe, Cu, Mn and K, Fe and Cu are the two with the highest risk for soils that accept OMW, considering that (i) iron toxicity corresponds to Fe levels > 100 mg kg^{-1} (ii) Cu levels > 3.0 mg kg^{-1} are characterized as high and that (iii) the majority of soils at OMW disposal areas have higher values than the thresholds for both metals (Table 3). Clin succeeded to retain high concentrations of Fe and Cu, which it is anticipated to be released slowly to soil solution. The results for these three metals were satisfactory for all plots without high variability among the different treatments. However, it seems that zeolite failed to increase Zn (Fig. 7d) and thus, leaching of Zn is likely to occur. Moreover, plots A seem to maintain significant values of Zn, which could be comparable to the values of the control plots.

Na (Fig. 8a) concentration was high only during the two first months after zeolite application, while after that period limited Na amounts were detected in pilot plots soils. The estimated values of the Exchangeable Sodium Percentage (ESP), which is defined as $[Na^+]$/[Total Exchangeable Cations], for all plots, except for plots B (5% zeolite of 0.8 - 2.5 mm), were higher than the threshold of 15%, however, these values became lower than the threshold during the next samplings (Fig. 8b).

Table 4. Available P, xchangeable Mg and Ca, $CaCO_3$ and pH of soil samples collected from the pilot zeolite area during the experiment

Date	***Available P, mg kg^{-1}***	***Exchangeable Mg, cmol kg^{-1}***	***Exchangeable Ca, cmol kg^{-1}***	***$CaCO_3$ %***	***pH***
January 14	264±13	6.3±0.3	51±5	12±2	7.6±0.2
March 14	150±9	4.0±0.2	41±3	20±3	7.5±0.1
May 2014	327±15	5.1±0.2	42±4	17±2	7.3±0.1
August 14	323±17	5.7±0.3	46±4	15±1	7.6±0.2
November 14	334±12	6.9±0.4	45±3	13±2	8.4±0.2
January 15	403±18	6.9±0.5	51±4	13±3	7.6±0.1
May 15	409±15	5.3±0.3	49±3	15±2	7.5±0.2
July 15	379±18	5.8±0.2	52±4	10±2	7.5±0.1
Plots B					
January 14	279±14	6.4±0.3	48±2	18±3	7.6±0.2
March 14	226±12	4.2±0.1	47±3	19±2	7.6±0.1
May 2014	206±14	3.7±0.1	39±3	17±2	7.6±0.1
August 14	452±15	5.6±0.3	36±2	18±1	7.9±0.2
November 14	331±13	6.2±0.3	37±4	17±2	7.9±0.2
January 15	457±16	6.8±0.4	44±3	21±3	7.8±0.2
May 15	400±19	5.7±0.3	42±2	15±2	7.5±0.2
July 15	456±21	5.7±0.2	44±3	18±1	7.4±0.1
Plots C					
January 14	201±15	5.5±0.2	35±3	16±2	7.7±0.2
March 14	171±13	5.1±0.3	44±3	15±2	7.7±0.1
May 2014	200±12	5.4±0.2	51±4	18±3	7.6±0.3
August 14	387±16	5.7±0.3	38±4	18±1	7.8±0.2
November 14	216±10	6.7±0.4	36±4	24±3	7.7±0.1
January 15	449±18	6.5±0.3	44±1	26±3	8.0±0.3
May 15	389±15	5.5±0.2	36±2	25±2	7.8±0.2
July 15	459±17	6.7±0.4	40±3	17±1	7.4±0.2
Plots D					
January 14	187±17	4.8±0.2	37±3	18±2	7.7±0.2
March 14	205±12	3.9±0.1	41±4	23±2	7.5±0.1
May 2014	331±14	4.0±0.3	40±3	21±1	7.5±0.2
August 14	409±20	4.5±0.2	34±3	23±3	7.9±0.3
November 14	250±11	5.6±0.3	36±2	26±2	7.8±0.2
January 15	354±15	6.1±0.3	34±2	25±1	8.0±0.3
May 15	491±18	4.9±0.2	33±1	21±2	8.0±0.2
July 15	450±19	6.2±0.4	39±3	19±2	7.7±0.2
Control Area					
January 14	450±21	11±1	77±5	27±3	6.7±0.1
March 14	390±17	8.0±0.6	71±3	29±3	7.6±0.2
May 2014	294±15	7.5±0.5	42±4	34±3	7.7±0.1
August 14	162±10	7.1±0.4	46±3	30±2	7.8±0.2
November 14	201±13	7.3±0.4	55±3	26±2	7.5±0.2
January 15	220±14	9.5±0.6	65±4	25±2	7.6±0.1
May 15	430±19	8.0±0.7	45±4	26±3	6.9±0.1
July 15	240±15	6.9±0.4	48±3	28±4	7.7±0.1

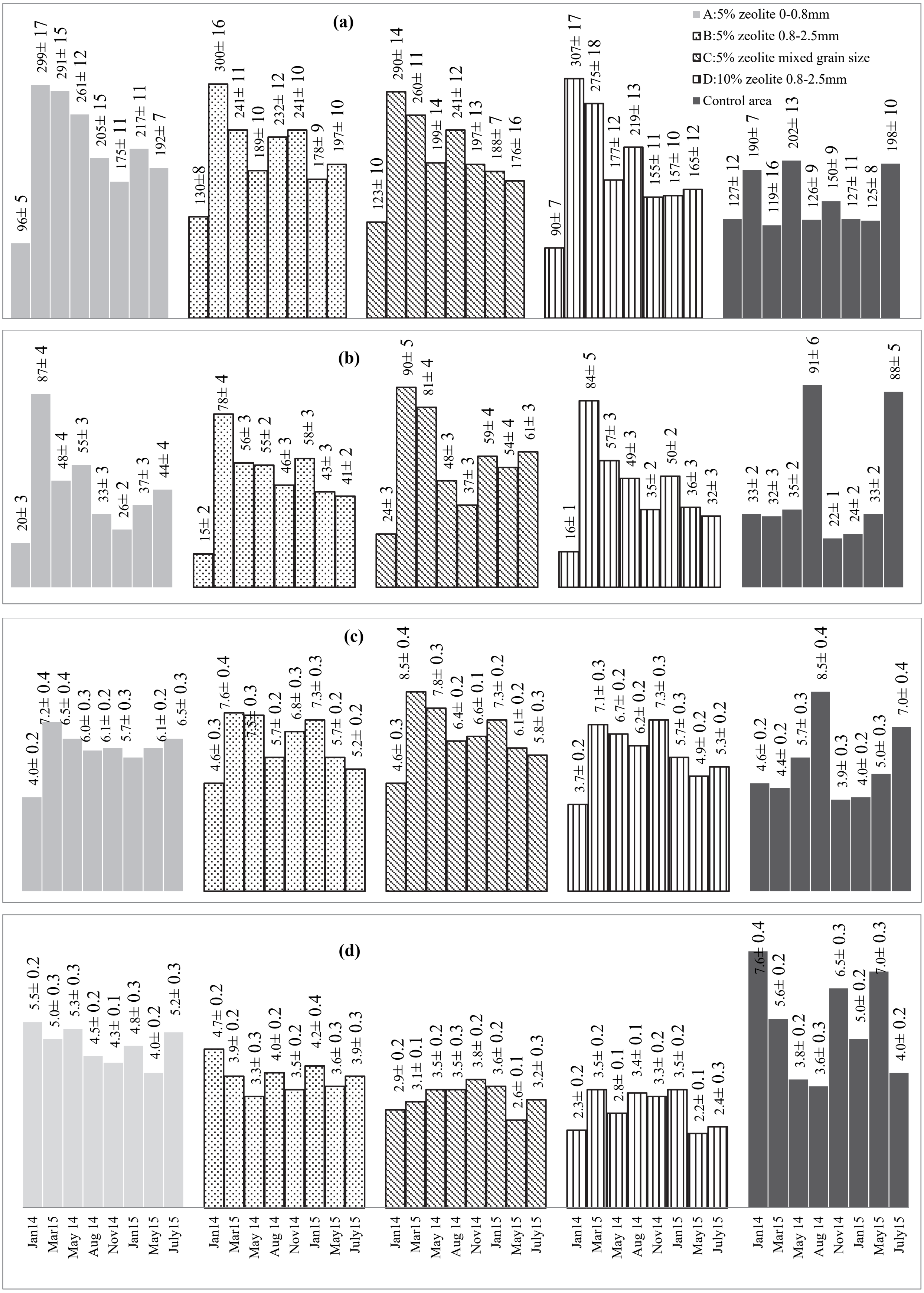


Fig. 7. (a) Available Fe (mg kg^{-1}); (b) available Mn (mg kg^{-1}); (c) available Cu (mg kg^{-1}); and (d) available Zn (mg kg^{-1}), of soil samples collected from the pilot zeolite area in relation to zeolite ratios and sampling dates

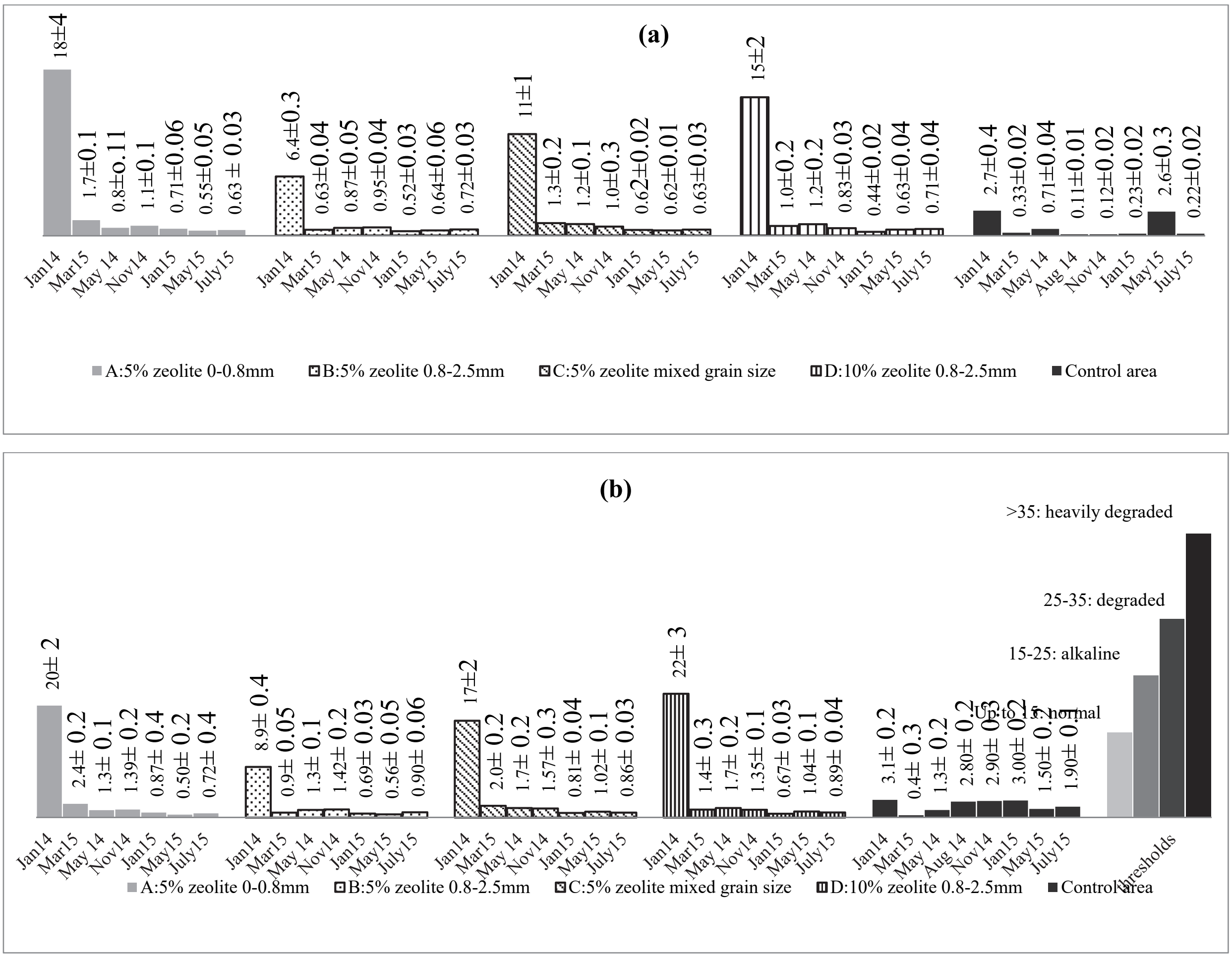


Fig. 8. (a) Exchangeable Na (cmol kg^{-1}); (b) ESP (%) of soil samples collected from the pilot zeolite area in relation to zeolite ratios and sampling dates

The final results indicate that Clin retained some of the waste constituents, preventing their leaching through soil layers. This behavior is typical for natural zeolites and especially Clin, while the retained ions could be released again in the soil environment, but their release is slow and controlled by zeolite properties and by their concentration in soil solution (Zorpas, 2008; Doula et al., 2012). As 75% of soil in Southern Europe has low organic matter as well as low content of organic carbon (less than 2% in a surface soil horizon from 0 to 30 cm) (EU, 2001), the disposal of OMW could be considered as beneficial to soils poor in organic matter (Martinez-Mena et al., 2002).

Zeolites, in general, have enormous CEC and expectedly attract positive-charged ions and, therefore, are widely used for sequestration of cations and cationic pollutants (EU, 2001). Natural and artificial zeolites increase ion-exchange capacity in soils, and allows to adsorb in the framework cavities the cations as pollutant metal ions (Zorpas et al., 2008; Doula et al., 2012). The fact that soil EC remained low is additional evidence that, despite the increase in exchangeable cations and available metals contents in soil, as recorded during this experiment, these amounts do not increase soil electrical conductivity because ions are held on or inside the zeolite framework.

Although this paper does not examine any economic factors it can be stated that from the economic point of view, it should be noted that Clin used as soil additive is also a cost-effective technique that can be easily applied and requires no specific machinery and non-skilled personnel. The total costs mainly cover: (i) the cost of the Clin (100 - 200 € t^{-1}), (ii) laboratory analysis, (iii) infrastructures, equipment (machinery) cost, (iv) employees cost, (v) cost for water supply (which however are considered very low to zero). It is estimated that the proposed solution per 1 ha is up to 68000 € or 27.8 € m^{-3} of treated soil and in total depth no more than 25 cm. Nevertheless, it is important to mention that in insular communities which no free spaces are available and due to the seasonality of the waste the disposal area is in the range of 0.1-0.2 ha.

4. Conclusions

Clinoptilolite could be an effective soil additive for areas where OMW surface disposal degrades soil quality. Uncontrolled disposal of OMW causes many disadvantages to the soil; some of them could be addressed by the use of clinoptilolite (metals removal etc). The results obtained from the pilot area studied, indicate that the use of Clin as soil additive optimized and control soil organic matters well as nitrogen forms (i.e NH_4) due to the continual and uncontrolled disposal of OMW. Furthermore, the addition of Clin, resulted in reduction in soil EC, while at the same time decreased the excess leaching of many inorganic waste's constituents (i.e. K, Fe, Mn, Cu) due to the retention of these cations by the mineral.

However, no substantial reduction was detected for soil available P and polyphenols content although the use of 10% zeolite could result in reduction of polyphenols. The final results indicated that leaching of Zn to deeper soil layers may be observed due to low concentrations of the mineral after the addition of Clin. In this case, the use of Clin in dust form could be more effective in immobilizing Zn by the mineral. Ca and Mg were found to decrease also due to the addition of zeolite with subsequent decrease in soil $CaCO_3$.

However, no significant change (increase or reduction) was recorded for soil pH. Sodium toxicity should always be subject of concern when zeolites are used for soil remediation. Nevertheless, results indicated that increased release of Na occurred during the first two months after the application.

The proposed technique is considered to be cost effective and Clin could be used in heavy polluted soils to improve their quality.

References

Al-Busaidi A., Yamamoto T., Inoue M., Eneji A.E., Mori Y., Irshad M., (2008), Effects of zeolite on soil nutrients and growth of barley following irrigation with saline water, *Journal of Plant Nutrition*, **31**, 1159-1173.

APHA, AWWA-WPCF, (1985), Standard methods for the examination of water and wastewater, American Public Health Association, Washington, U.S.A.

Arienzoa M., Christena E.W., Quaylea W., Kumarc A., (2009), A review of the fate of potassium in the soil–plant system after land application of wastewaters, *Journal of Hazardous Material*, **164**, 415-422.

Box J.D., (1983), Investigation of the Folin–Ciocalteu phenol reagent for the determination of polyphenolic substances in natural waters, *Water Research*, **17**, 511-525.

Cereti C.F., Rossini F., Federici F., Quaratino D., Vassilev N., Fenice M., (2004), Reuse of microbially treated olive mill wastewater as fertiliser for wheat (*Triticum durum* Desf.), *Bioresource Technology*, **91**, 135-140.

Costa C.N., Savva P.G., Zorpas A.A., (2012), *Catalytic Properties of Zeolites,* In: *Handbook on Natural Zeolite*, Inglezakis J.V, Zorpas A.A (Eds), Bentham Science Publishers, The Netherlands, 66-85.

Dias A.A., Bezerra R.M., Pereira A.N., (2004), Activity and elution profile of laccase during biological decolorization and dephenolization of olive mill wastewater, *Bioresource Technology*, **92**, 7–13.

Doula M.K., (2006), Removal of Mn^{2+} ions from drinking water by using Clinoptilolite and a Clinoptilolite-Fe oxide system, *Water Research*, **40**, 3167-3176.

Doula M.K., (2007), Synthesis of a Clinoptilolite-Fe system with high Cu sorption capacity, *Chemosphere*, **67**, 731-740.

Doula M.K., Elaiopoulos K., Kavvadias V., Mavraganis V., (2012), Use of clinoptilolite to improve and protect soil quality from the disposal of olive oil mills wastes, *Journal of Hazardous Material*, **207-208**, 103-110.

Doula M.K., Kavvadias V.A., Elaiopoulos K., (2012), *Zeolites in Soil Remediation Processes,* In: *Handbook on Natural Zeolite*, Inglezakis J.V, Zorpas A.A (Eds), Bentham Science Publishers, The Netherlands, 519-568.

EU, (2001), Organic Matter in Soils of Europe: Present status and future trends, European Commission Directorate General JRC, Join Research Centre, Institute for Environment and Sustainability, European Soil Bureau, 10-15, On-line at: https://core.ac.uk/download/pdf/38615475.pdf

Gohary-El F.A., Badawy M.I., El-Khateeb M.A., El-Kalliny A.S., (2009), Integrated treatment of olive mill wastewater (OMW) by the combination of Fenton's reaction and anaerobic treatment, *Journal of Hazardous Material*, **162**, 1536-1541.

Goula K.A., Lazarides N.H., (2015), Integrated processes can turn industrial food waste into valuable food by-products and/or ingredients: The cases of olive mill and pomegranate wastes, *Journal of Food Engineering*, **167**, 45-50.

Inglezakis V.J., Moreno J.L., Doula M.K., (2012), Olive oil waste management EU legislation: Current situation and policy recommendations, *International Journal of Chemical and Environmental Engineering System*, **3**, 65-77.

ISO/IEC11260, (1994), Soil quality - Determination of effective cation exchange capacity and base saturation level using barium chloride solution, 1-10. International Organization for Standardization, Geneva, Switzerland, On line at: https://www.iso.org/standard/60566.html.

ISO/IEC 11261, (1995), Soil quality - Determination of total nitrogen - Modified Kjeldahl method, 1-3. International Organization for Standardization, Geneva, Switzerland, On line at: https://www.iso.org/standard/19239.html.

ISO/IEC 11465, (1993), Soil quality - Determination of dry matter and water content on a mass basis - Gravimetric method, 1-3. International Organization for Standardization, Geneva, Switzerland, On line at: https://www.google.ro/url?sa=t&rct=j&q=&esrc=s&source=web&cd=1&cad=rja&uact=8&ved=2ahUKEwjWzpDTgpfjAhVDL1AKHXp8AlAQFjAAegQIARAB&url=https%3A%2F%2Fwww.iso.org%2Fstandard%2F20886.html&usg=AOvVaw3GUq0UpapgUcoE5Q5esfdd.

ISO/IEC 14235, (1998), Soil quality - Determination of organic carbon in soil by sulfochromic oxidation, 1-5. International Organization for Standardization, Geneva, Switzerland, On line at: https://www.iso.org/standard/23140.html.

ISO/IEC 14870, (2001), Soil quality - Determination of trace elements by buffered DTPA solution, 1-4. International Organization for Standardization, Geneva, Switzerland, On line at: https://www.iso.org/standard/40653.html.

Jarboui R., Sellami F., Kharroubi A., Gharsallah N., Ammar E., (2008), Olive mill wastewater stabilization in open-air ponds: Impact on clay–sandy soil, *Bioresource Technology*, **99**, 7699-7708.

Karaouzas I., Cotou E., Albanis T., Kamarianos A., Skoulikidis N., Giannakou U., (2011), Bioassays and biochemical biomarkers for assessing olive mill and citrus processing, wastewater toxicity, *Environmental Toxicology*, **26**, 669–676.

Kavvadias V., Doula M.K., Komnitsas K., Liakopoulou N., (2010), Disposal of olive oil mill wastes in evaporation ponds: Effects on soil properties, *Journal of Hazardous Material*, **182**, 144-155.

Komilis D.P., Karatzas E., Halvadakis C.P., (2005), The effect of olive mill wastewater on seed germination after various pretreatment techniques, *Journal of Environmental Management*, **74**, 339-348.

Liang Y., Zhang X., Dai D., Li G., (2009), Porous biocarrier-enhanced biodegradation of crude oil contaminated soil, *International Biodeterioration & Biodegradation*, **63**, 80-87.

Mahmoud M., Janssen M., Haboub N., Nassour A., Lennartz B., (2010), The impact of olive mill wastewater application on flow and transport properties in soils, *Soil and Tillage Research*, **107**, 36–41.

Martinez-Mena M., Alvarez-Rogel J., Castillo V., Albaladejo J., (2002), Organic Carbon and nitrogen losses influenced by vegetation removal in a semiarid Mediterranean soil, *Biogeochemistry*, **61**, 309-321.

Mohawesh O., Mahmoud M., Janssen M., Lennartz B., (2014), Effect of irrigation with olive mill wastewater on soil hydraulic and solute transport properties, *International Journal of Environmental Science Technology*, **11**, 927-934.

Pavlidou A., Anastasopoulou E., Dassenakis M., Hatzianestis I., Paraskevopoulou V., Simboura N., Rousselaki E., Drakopoulou P., (2014), Effects of olive oil wastes on river basins and an oligotrophic coastal marine ecosystem: A case study in Greece, *Science of the Total Environment*, **497–498**, 38–49.

Peri C., Proietti P., (2014), *Olive mill waste and by-products.* In: *The Extra-Virgin Olive Oil Handbook*, John Wiley and Sons, 283-302.

Szollosi-Mota A., Prodan M., Ghicioi E., Nalboc I., Moldovan C., (2017), Heavy metals removal from mining drainage acid water by use of natural zeolites, *Environmental Engineering and Management Journal*, **16**, 1383-1388.

Vlyssides A.G., Loizidou M., Zorpas A.A., (1999), Characteristics of solid residues from olive oil processing as a bulking material for co-composting with industrial wastewater. *Journal of Environmental Science and Health*, **3**, 737-748.

Vlyssides A.G., Zorpas A.A., Karlis P., Zorpas A.G., (2000), Description of a Pilot Plant for the Co-Composting of the Solid Residue and Wastewaters from the olive oil Industry, *Hungarian Journal of Industrial Chemistry*, **2**, 59-64.

Zorpas A.A., (2008), Sewage sludge compost evaluation in oats, pepper and eggplant cultivation, *Dynamic Soil – Dynamic Plants, Global Science Book*, **2**, 103-109.

Zorpas A.A., (2009), Heavy metals leachability before, during and after composting of sewage sludge with natural zeolite, *Desalination and Water Treatment*, **8**, 256-262.

Zorpas A.A., (2012), *Contribution of Zeolites In Sewage Sludge Composting.* In: *Handbook on Natural Zeolite*, Inglezakis J.V, Zorpas A.A (Eds), Bentham Science Publishers, The Netherlands, 182-199.

Zorpas A.A., (2015), Sustainable waste management through end-of-waste criteria development, *Environmental Science and Pollution Research*, DOI 10.1007/s11356-015-5990-5

Zorpas A.A., Costa N.C., (2010), Combination of Fenton Oxidation and Composting for the treatment of the olive solid residue and the olive mile wastewater from the olive oil industry in Cyprus, *Bioresource Technology*, **101**, 7984-7987.

Zorpas A.A., Inglezakis V., Stylianoy M., Voukkali I., (2009), Sustainable treatment method of a high concentrated NH_3 wastewater by using natural zeolite in closed-loop fixed bed systems, *Open Environmental Journal*, **3**, 70-76.

Zorpas A.A., Loizidou M., (2008), Sawdust and natural zeolite as a bulking agent for the improving the quality of a co-composted product which it based on anaerobically stabilized sewage sludge, *Bioresource Technology*, **99**, 7545-7552.

Zorpas A.A., Tzia N., (2008), The implementation of a new ISO 22000 in the Cyprus olive oil industry, *WIT Transactions on Information and Communication Technologies*, **39**, 261-274.