Annals of Agrarian Science

Journal homepage: http://journals.org.ge/index.php

Physical Properties and Ion Mobility Assays in Technosols Designed for Soil Restoration of Extractive Activities

M.M. Jordán[a]; E. García-Sánchez[a], M.B. Almendro-Candel[a], J. Bech[b]

[a]Department of Agrochemistry and Environment (GEA-UMH). University Miguel Hernández- Avda. de la Universidad s/n, Elche (Alicante), 03202, Spain

[b]Soil Science Laboratory, Faculty of Biology, University of Barcelona-Avda. 643, Diagonal,Barcelona, 08028, Spain

Received: 22 January 2020; accepted: 19 March 2020

A B S T R A C T

The rehabilitation technologies in areas degraded by extractive activities require the use of their own mine spoils. Reducing deficiencies in bulk density and aggregate stability, organic matter, and nutrients with a contribution of treated sewage sludge is proposed. This experiment was based on a controlled study using percolation columns. The assays was done using two mine spoils, both very rich in calcite. Two sewage sludge doses were undertaken (30,000 and 90,000 kg/ha of sewage sludge compost) in addition to a different mine spoils used as substrates. Irrigation water was provided by a device that simulated short duration rain. The leached water was collected 24 hours after the last application. Electrical conductivity, pH and the ions nitrate, ammonium, phosphate, sulfate, and chloride were determined. The experiment saw the bulk density decrease and the aggregate stability increase, thereby improving the structure. Significant nitrate concentrations appeared that may pose an environmental contamination risk. The resulting values for each irrigation application, the relationship between parameters, and the environmental risk are discussed.

Keywords: Sewage sludge, Irrigation, Ion mobility, Leachates, Bulk density

*Corresponding author: Jaume Bech; E-mail address: jaumebechborras@gmail.com

Introduction

From the ecological point of view, the restoration of extensive areas degraded by mining activities, the use of their own waste materials is required [1-4]. These materials do not possess the necessary fertility to ensure a successful process of restoration (implementation of adequate plant cover). Therefore, it requires the addition of organic amendments to achieve efficient substrate [5]. The obligation to restore abandoned mine and the correct application of biosolids is guaranteed by the legislation on waste management, biosolids and soil conservation [5]. Technosols are one of the latest additions to the World Reference Base for Soil Resources [6]. This new reference soil group contains a large range of artifacts and materials of natural and anthropic origin. They include a variety of refuse-based soil-like mine spoils, landfills, cinders, or sludge, whose properties and pedogenesis are dominated by their technical origin [7]. An adequate technosol selection can constitute a valuable and cost-effective solution for soil remediation and waste management [7]. Sewage sludge application in restoration has demonstrated its efficiency in previous studies [5, 8-10]. The use of treated sewage sludge can be a guarantee of success in the rehabilitation of areas affected by extractive activities, but it is important to preserve the environment with less risk of contamination of groundwater [10].

The experimentation was carried out on a controlled study using percolation columns. PVC pipe with a 10.5-cm interior diameter cut into 15-cm length pieces was used to make them. Two of these pieces were then stacked to construct each of the fifteen 30-cm tall columns (Fig. 1). Two treatments and a control were applied, which depended upon the quantity of sludge applied (Table 1 and Table 2). The sludge was applied on the surface and mixed with the soil, simulating a plowing or tilling action, producing a homogenous mixture within the uppermost 15 cm of soil.

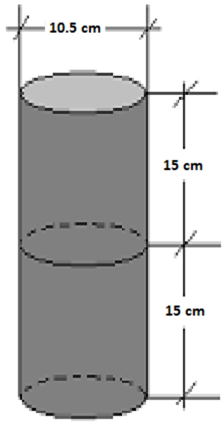

Fig. 1. Percolation columns used in the experiment

Table 1. *Quantity of sewage sludge applied in each treatment*

Sewage sludge quantity (kg/ha)	Designation
0	0
30,000	3
90,000	9

Table 2. *Experimental design and identifying symbols*

Symbol	Material contents
Z_0	30 cm column filled with aggregate (coarse).
D_0	30 cm column filled with degraded soil (fine).
$(Z+D)_0$	30 cm column filled from 0-15 cm with degraded soil and 15-30 cm with aggregate.
D_3	30 cm column filled with degraded soil. Sewage sludge dose (30,000 kg/ha) homogenous mixture first 15 centimeters.
D_9	30 cm column filled with degraded soil. Sewage sludge dose (90,000 kg/ha) homogenous mixture first 15 centimeters.
$(Z+D)_3$	30 cm column filled from 0-15 cm with degraded soil and 15-30 cm with aggregate. Sewage sludge dose (30,000 kg/ha) homogenous mixture first 15 centimeters.
$(Z+D)_9$	30 cm column filled from 0-15 cm with degraded soil and 15-30 cm with aggregate. Sewage sludge dose (90,000 kg/ha) homogenous mixture first 15 centimeters.

The experiment was carried out using two types of wastes rich in calcite (75-90%). The first, poor in quality was characterized by a predominance of the coarse element fraction (up to 75% by weight) and by containing high percentages of sand (Z). The second residual material tested came from the extraction of limestone. This waste was formed by levels of intercalated materials and residues of degraded soils (D). This usually has high heterometric stoniness (up to 60%), and is richer in clays (approx. 25%). These materials were amended with the biosolid according to quarry restoration methodology [11]. The characteristics of the mineral substrata employed appear in Table 3.

Table 3. *Characteristics of the substrata used in the experiment*

Texture	Clay (%)	Silt (%)	Sand (%)
Aggregate	15.40	16.00	68.60
Degraded	21.37	26.00	52.63

Parameter	Z	D
pH	8.25	8.92
EC S/cm (25 ºC)	257.20	56.32
OM (%)	0.53	0.27
P (mg/kg DM)	2.04	2.07
Ca (g/kg DM)	3.37	3.26
Mg (mg/kg DM)	134.13	337.57
Na (mg/kg DM)	222.15	63.27
K (mg/kg DM)	34.66	64.31
Fe (mg/kg DM)	2.25	1.48
Cu (mg/kg DM)	0.29	0.18
Mn (mg/kg DM)	2.08	1.07
Zn (mg/kg DM)	0.73	0.36
N (%)	0.03	0.02
$CaCO_3$ (%)	45-75%	55-70%
Act. Limestone (%)	18%	15%

The substratum used has a basic pH; therefore, it is a soil with an alkaline reaction. This means that most nutrients may have availability problems, making acidifying amendments necessary to lower the pH, facilitate element mobility, and improve the soil structure. The substratum has a relatively low nutrient content. Ca^{2+} is the element found in the greatest proportion within the soil solution. K^+ and Na^+ concentrations are moderate. This is reflected in the soil's electrical conductivity because these cations, especially Na^+, are very soluble and have considerable repercussions on this measurement when their concentrations are high. The equivalent calcium carbonate content is very high, as is typical for these types of tailings. The organic matter content is very low, just like that for assimilable phosphorous and Kjeldahl nitrogen compared with the desired normal content for a cultivated soil. With respect to the composition of assimilable nutrients (extract with ammonium acetate and DTPA), it is shown that, with the exception of Ca^{2+}, the remaining elements are found at low or very low levels, with iron, among others, standing out. Iron availability is normally low in limy soils whose cultivation practically makes any inorganic form of this metal inassimilable [12].

The biosolid used in this experiment comes from a wastewater treatment plant located near Aspe (Alicante). Prior to the composting process, the sludge needs to be mixed with a bulking agent, a supporting structure that favors aeration, absorbs humidity, and furthermore contributes carbon. Chopped hay and sawdust are used as the bulking agent, and silos exist for their storage. Hay favors aeration, sawdust absorbs humidity, and both materials constitute sources for carbon. The composition by volume of the sludge-bulking agent mixture is 50% sludge, while the remaining 50% is 1/4 hay and 3/4 sawdust. This sludge-bulking agent mixture progresses through the composting tunnel and is simultaneously homogenized by a tumbler, which in addition to permitting the progress and homogenization of the mixture, promotes its aeration. During the first weeks, the mixture is placed upon a porous base connected to an air injection system using fans or blowers, which maintains discontinuous forced aeration. Afterwards, the aeration is passive and natural.

For the sludge analysis, its total mineralization was carried out by electrothermal radiation (microwaves) in an acid medium. In the solution thus obtained, the solubilized elements except for nitrogen were assessed. This was determined by the Kjeldahl method, which quantifies the organic nitrogen and ammonium contents within the sample. The easily oxidizable organic carbon was calculated by sulfochromic digestion and subsequent assessment with Mohr's salt, an easily oxidizable organic matter by applying the 1.72 conversion factor, and the total by calcination in a muffle furnace at 500 ºC for 2-4 h.

As for macroelements, the sludge presents low contents of phosphorous and potassium, with medium contents for calcium and magnesium, all within the ranges cited by [13]. The total sodium content is of some importance, but cannot be considered dangerous for the soil. Analytically controlling the sludge at the time of its incorporation is important, especially with regards to sodium, as this element may cause soil salinity problems and alter its structure [14]. The C/N ratio is 12, indicating that the organic matter is partially mineralized and, therefore, the sludge can enhance soil fertility [15]. Many physical and chemical properties in soils amended with sludge, such as water adsorption, aggregate stability, contribution from N, P, and other nutrients for crop growth, depend, to some extent, upon the quantity of organic matter in the sludge that is added. Knowledge about the quantity of organic matter in the sludge can be used to estimate the quantities that must be applied to the soil [16]. Use sewage sludge and mine spoils as technosols constitute innovative strategies of waste management, whose application allowed the species growth and development [7]. This sewage sludge has an organic matter content that is very suitable for agricultural use (Table 4).

Table 4. *Sewage sludge composition (dry matter, DM) from the Aspe wastewater treatment plant*

Parameter	Value
Organic C (%)	44.4
Kjeldahl N (%)	3.7
C:N ratio	12
P (%)	0.29
K (%)	0.02
Ca (%)	0.09
Mg (%)	0.08
Fe (g/kg DM)	5.48
Cu (mg/kg DM)	289
Cd (mg/kg DM)	0.97
Ni (mg/kg DM)	18
Pb (mg/kg DM)	121
Zn (mg/kg DM)	768
Hg (mg/kg DM)	1.23
Cr (mg/kg DM)	21

2. Materials and methods

2.1. Irrigation

The soil contained in the columns was irrigated (8 applications) using tap water. The first five irrigations occurred every two weeks and the last three once per month. The irrigation applications lasted 6 months. Collection of the leached water was carried out 24 hours after the last application. The contribution of water was provided by a device that simulated short rainfall or a flood irrigation system that covered the surface and then percolated into the soil. It consists of a plastic recipient with holes punched in the bottom [10]. Water samples were taken from each one of them. Their saline characteristics were determined first, i.e., pH, electrical conductivity, the Na^+, K^+, Ca^{2+}, and Mg^{2+} cations, as well as the C^{l-}, $SO4^{2-}$, and HCO^{3-} anions [17].

2.2. Determination of some physical properties of the substratum

Bulk Density

Bulk density is defined as the ratio between the mass of the oven dry soil and the overall volume, which includes the volume of the particles and the porous space between them. It is dependent upon the soil particle densities (sand, silt, clay, and organic matter) and their type of packaging. Mineral particle densities are found within the range of 2.5 to 2.8 g/cm3, while organic particles are usually <1.0 g/cm3. The bulk density is a dynamic property that varies along with the structural conditions of the soil. It can serve as an indicator of the compaction and the restrictions to root growth (Table 5).

Table 5. *General relationship of soil bulk density to root growth based on soil texture*

Soil texture	Ideal bulk densities (g/cm^3)	Bulk densities that may affect root growth (g/cm^3)	Bulk densities that restrict root growth (g/cm^3)
Sands, loamy sands	<1.60	1.69	>1.80
Sandy loams, loams	<1.40	1.63	>1.80
Sandy clay loams, loams, clay loams	<1.40	1.60	>1.75
Silts, silt loams	<1.30	1.60	>1.75
Silt loams, silty clay loams	<1.40	1.55	>1.65
Sandy clays, silty clays, some clay loams (35-45% clay)	<1.10	1.49	>1.58
Clays (>45% clay)	<1.10	1.39	>1.47

Source: USDA (1999). Soil Quality Test Kit Guide

Measuring the bulk density in every case is important due to its great variability. Between an organic horizon and a very compact Bt horizon, the values may vary from 0.1 to 1.80 or even more grams per cubic centimeter; under these conditions, the errors that may occur in the estimated parameters from it can be enormous. Determining the bulk density may be done by different methods, but preferably two are used. The best way to determine the bulk density is by taking a fixed volume of undisturbed soil and weighing it once dry, after heating it at 105º C until it reaches a constant weight. To do this, a metallic cylinder with a volume close to 100 mL is usually used. Once it is full and flush at both ends, the contained soil is extracted. Its volume corresponds to that of the cylinder and therefore known; it is then dried and weighed. The density is determined by the ratio between the weight obtained and the corresponding volume. The main drawback to this system is the presence of stones, so this can only be used in non-stony soil, which unfortunately, is less common. In this case, using another system is more convenient, one that is less precise but easier. It involves taking aggregate from the soil, as large as possible, drying it, and weighing it to learn its mass. A string is tied to it and it is submerged into molten paraffin to coat and waterproof its surface; once solidified, it can be weighed once again. The wax-coated aggregate is introduced into a graduated cylinder containing a known quantity of water. The volume gain of the water as a consequence of the introduction of the aggregate corresponds to its volume. This way, the two parameters necessary for the density calculation are learned. Although the paraffin layer is very thin and its volume negligible, it can be estimated based on its density and the weight increase undergone by the aggregate following the waterproofing process. The main drawback of this method is that it cannot specify the volume of the cracks and interned voids. However, by wetting the soil, they all disappear; this serves to determine the behavior of moist soil.

Aggregate stability

Aggregate stability is a measure of the vulnerability of soil aggregates exposed to external disruptive forces. Soil aggregates consist of diverse particles that are bound to one another. Aggregates that resist the forces of water are called water-stable aggregates (WSA). In general, the higher the percentage of stable aggregate, the lower the soil erodibility. Soil aggregates are products of the soil microbial community, the organic and mineral components in the soil, the nature of the plant communities on the surfaces, and the ecosystem history. They are important in the movement and storage of soil water, erosion, root development, and microbial activity. The destruction of aggregates is the first step towards the development of crusting and surface sealing, which prevent water infiltration and increase erosion. Soil aggregation can vary over certain periods of time, such as a season or a year. Aggregates can form, disintegrate, and re-aggregate periodically. Aggregates improve soil quality by:

- Protecting the organic matter trapped in the aggregates from exposure to air and microbial decomposition.
- Decreasing soil erodibility.
- Increasing the movement of water and air (aggregates increase the amount of large pore space), thus improving the physical environment for root development and the habitat for soil organisms.

Determining the percentage of stable aggregates in the soil was performed by an artificial rain simulator according to the method described by [18].

2.3. Leachates

pH and electrical conductivity

Determining the electrical conductivity is performed by an electrical conductivity meter, which incorporates a conductivity cell, considering 25 ºC as the reference temperature, according to current analysis methods [19]. Measuring the electrical conductivity depends upon the type of ions present in the sample, their concentration, and the temperature at which the reading is taken.

Anions

The chloride content was determined by the Mohr method, based on the formation of silver chloride, an insoluble salt, detecting the turning point by the appearance of a red precipitate of Ag_2CrO_4, a compound used as an indicator [19]. Sulfates were determined following the nephelometric technique [20]. The nitrate content is determined by second-derivative ultraviolet spectroscopy [21].

The method for the determination of phosphorous is based on the formation of a phosphomolybdic complex in an acid medium, reduced by ascorbic acid, producing a blue coloration that is measured at 825 nm. The phosphorous is measured as a phosphate ion.

Cations

The method for determining ammonium is based on the development of indophenol blue by reaction of ammonium ions treated with a solution of sodium hypochlorite and phenol in the presence of nitroprusside acting as a catalyst. The Na^+, K^+, Mg^{2+}, and Ca^{2+} ions are measured directly in the sample or in appropriate dilutions by atomic emission spectrophotometry in the case of the first two ions, and by atomic absorption for the last two [10].

2.4. Linear regression analysis

Simple linear ***regression*** analysis was applied to the developed experimental data. It aims to predict and/or estimate the values of the dependent variable based on obtaining a linear function of the independent variable. Mathematically, the linear model or regression line is the following:

$$Y = a + b * X$$

Where *a*: cutoff point of the line with the response variable *Y*
Y: intercept
b: slope of the line, called the regression coefficient: the average rate of increase or decrease in Y caused by a unit increase in X.

Analyzing the degree of linear association between the dependent and independent variables is necessary. To do this, among other statistics that permit assessing the goodness of fit of the data to the linear regression model, we have used:

Simple linear correlation, *r*, or what is also called the Pearson linear correlation coefficient, measures the degree of linear association between the variables, i.e., the joint variation of the two variables. This measure is unitless and independent of the scale at which the variables are measured. Its interpretation is very easy because it always takes values between 1 (strong positive linear association) and -1 (strong negative linear association). When the *r* values approach 0, no linear association exists between the considered variables, and therefore, determining the model and linear regression equation will be meaningless.

There may be an interesting and informative nonlinear relationship of one variable given the other. Consequently, basing the evaluation of the relationship exclusively on *r* is neither safe nor reasonable. In this sense, it is very convenient to accompany calculating *r* with the representation of the point cloud, since a visualization of the relationship between the variables will be obtained. A defined point cloud and a proximity between points close to the trend line that represents the correlation will indicate an acceptable relationship between the variables.

The squared correlation coefficient (R^2) represents the proportion of the variation of a variable that is explained by its linear association with another variable.

3. Results and discussion

3.1. Physical properties

The bulk density and percentage of stable aggregates have been determined as physical properties that can be modified following the application of organic amendments to the soil like is sewage sludge.

With respect to the substrata without amendment, aggregate (Z_o), degraded (D_o), and a mixture of aggregate and degraded $(Z+D)_o$, the results indicate that substratum Z_o has the lowest bulk density, logically due to its much thicker texture that is going to favor the availability of air voids in the column, decreasing the mass/volume ratio. As seen in Fig. 2, the sludge application decreases the bulk density in the distinct substrata tested with respect to the control, with the decrease being greater the greater the sludge dose. The organic content of the applied residue is going to improve the substratum structure by favoring the formation of pores that contribute to the bulk density decrease [22]. High doses of sludge (90,000 kg/ha) obtain a bulk density inferior to 1.4 g/cm^3, a value recommended by the USDA [23]. for sandy loams and loams (Table 5). Bulk density values greater than 1.6 g/cm^3 can affect root growth and even restrict it (Table 5).

Figure 3 shows that the control substrata used have a relatively low percentage of stable aggregates. The application of sludge significantly increases the percentage of stable aggregates, with this increase much larger for the greater application rate (90,000 kg/ha). The increase of organic matter

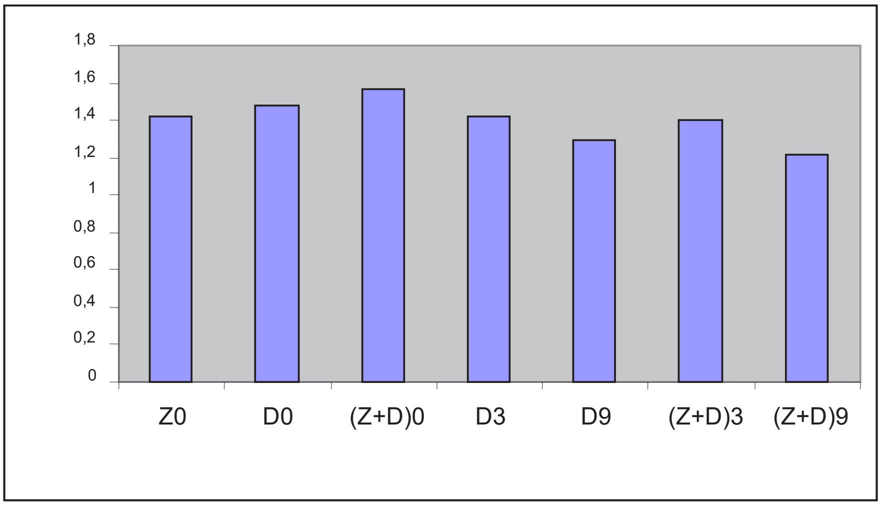

Fig. 2. *Bulk density (g/cm³) for the different substrata used*

in the soil will improve numerous properties thereof, among which all those related with the structure, like bulk density, aggregate stability, porosity, etc., can be highlighted. The improved soil structure decreases its vulnerability to degradation processes such as erosion and compaction. Nevertheless, no cases reached the values recommended by the USDA [23] for soils with a clay fraction percentage around 15%, which was situated between 65-70%. Considering the percentage of organic matter in the substrata, the aggregation percentage should have been 53% for the case of D_3 and 70% for the case of D_9 (USDA, 1999). During our experiment, these values were not reached (Fig. 3). It must be kept in mind that aggregate stability should increase over time.

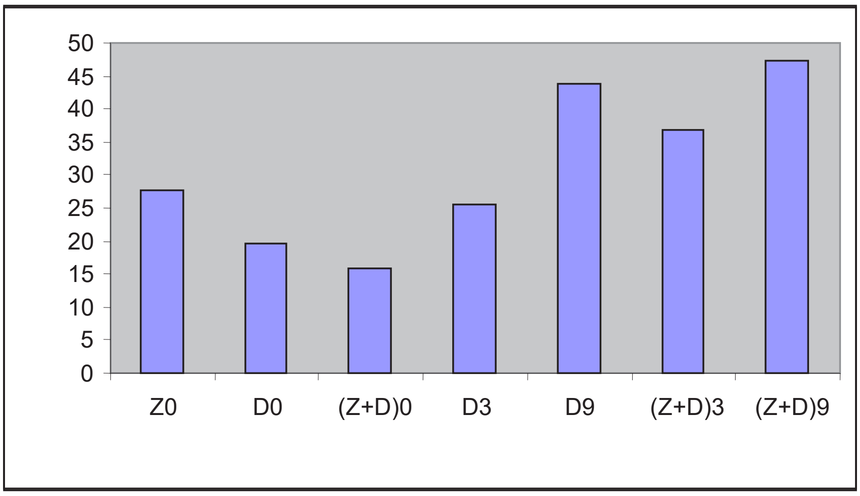

Fig. 3. *Aggregate stability (%) in the different substrata used*

3.2. Leachate analysis

The wash water of the mineral substratum can serve as a point of reference for possible contamination that may appear in groundwater when sewage sludge is applied as an amendment [5].

pH

No significant changes in the pH were produced between treatments; an acidifying trend was only seen in the first and third sampling in the treatments. Over time, it was observed that the pH values were more similar to that of the irrigating water before being added to the soil. The lowest pH values coincided with the beginning of the experiment (incorporation of residual matter and beginning of irrigation) and when the greatest degradation of the organic matter appears to have occurred, between the second and third irrigation.

Electrical conductivity

An increase in this property was observed in the water collected from the columns treated with sludge with respect to the control. This is due to the resulting wash of the soluble salts that the biosolid applied to the soil provided. The electrical conductivity values were closely related with the dose of biosolid applied, above all during the first 3 consecutive irrigation applications. However, the electrical conductivity values were only worrisome during the first three irrigation applications; beginning with the fourth and particularly the fifth ones, the electrical conductivity values stabilized as the preceding irrigations washed out the salts.

Inorganic nitrogen forms

Two of the three inorganic forms of nitrogen in the leachates are discussed: nitrates and ammonium. The nitrites analyzed in the wash water were very close to the detection limit of the technique used. Their results are not discussed because they were not significant.

An increase in nitrate concentration was observed in the water resulting from the soils treated with sludge with respect to the control soil. The treatments with high sludge doses (90,000 kg/ha) are those that contributed higher NO_3^- contents to the water. The highest NO_3^- concentration in the leachates occurred in irrigations 1, 2, and 3 (2500-300 mg/L). From the fourth irrigation application onward, the wash of this anion was much scarcer. The nitrates exceeded the recommended values in the two treatments. In any case, these high nitrate concentrations would drop with the restoration and development of vegetative cover, which would assimilate a large portion of the nitrates, thereby reducing the possible risk of groundwater contamination.

The values obtained for ammonium were only significant for the first irrigation application. This cation increased with the biosolide dose, whose differences decreased over time. The ammonium quantities were far inferior to those obtained for NO_3^-, which is due to higher fixation of the NH_4^+ in the mineral substratum and its participation in the nitrification process to produce the more oxidized forms of the nitrogen.

Anions

A certain tendency was observed in the phosphorus to increase with the sludge dose treatment. The highest values were obtained in the columns filled with degraded soil (D) and with the applications equivalent to 90,000 kg/ha of composted and treated sludge. The recommended concentration limits were not exceeded in any treatments. High natural limestone in this soil impeded in part the displacement and loss of soil phosphorus (calcium phosphate precipitation).

Chlorides and sulfates are involved in mineral nutrition of plants. Furthermore, they are very relevant quality control parameters of water. Significant differences appeared in the chloride anions between the treatments with sludge and the control. Quite possibly, the most influential factor when determining the Cl^- in the leachates is the contribution from the sewage sludge, without forgetting that the substrata used (aggregate and degraded soil) contains abundant salts. In fact, in the first two irrigation applications, high chloride values resulted in the control columns with the presence of aggregate (Z or Z+D) with lower values in the control columns filled with degraded soil (D). This observation demonstrates the contribution of chlorides by the wash of the aggregate (Z) used as a mineral substratum. The chlorides were practically completely washed out in the first three irrigation applications. In the case of sulfates, an increase was noted with the treatment that decreased over time, whose highest values were reached in the second irrigation application. This circumstance corroborates the fact that the organic sulfur may have undergone organic matter mineralization processes and appeared in the leachates most significantly in the third sampling.

Cations

From the environmental point of view, the concentrations of Ca, Mg, Na and K in the leachates pose no risk. The contribution from soluble K^+ with the sludge does not appear to produce an increase of this element in the leachates. It is possible that the clayey nature of this degraded soil limits the displacement and loss of this nutrient that fixes relatively easily to the clay minerals. In the sodium, a clear increase was noticed in the first and second irrigation application with the treatment that was not significant for the remaining samplings. There was a tendency for its leaching to increase over time. The calcium seems to increase with the treatment and the sludge dose applied. Over time, its tendency is to decrease. The soil reaction with the sludge appears to have increased the presence of soluble Ca^{2+}, as it appeared in the leachates in considerable concentrations. The magnesium increased significantly with the treatment, and diminished with the passing of time.

3.3. Correlations

In this section, the linear regressions obtained by relating some parameters with others are analyzed, which gives us an idea about the linear relationship existing between the variables being studied. To do this, we used Pearson's linear correlation coefficient (r) that measures the degree of association between the variables, i.e., the joint variation that exists between the two variables. Its value is comprised between 1 (strong positive linear association) and -1 (strong negative linear association). When the *r* values approach 0, this means that no linear association exists between the considered variables. Since not all the obtained correlations produced significant results, we will only discuss those that did. Although there is no wide dispersion in the results, as can be seen in the different graphs, the linearity is more pronounced in the lower values, where a larger quantity of data exists. It would be desirable for future research to complete these correlations using a wider range of values.

The electrical conductivity correlated well with the alkaline and alkaline earth elements analyzed in the wash water, with the exception of K^+ (Fig. 4, 5 and 6). In the case of Ca^{2+}, this correlation was excellent (Figure 4). It is obvious that the washed Ca^{2+} comes from both the substratum used as well as the sludge applied as organic amendment.

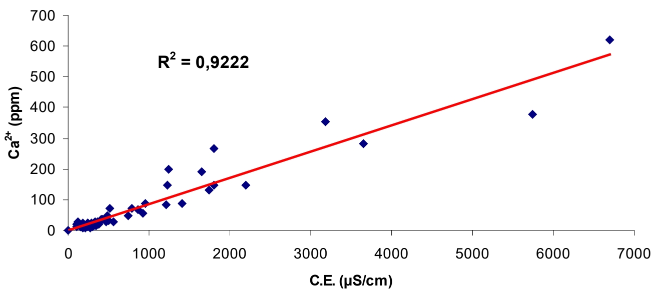

Fig. 4. *Correlation between the electrical conductivity and calcium*

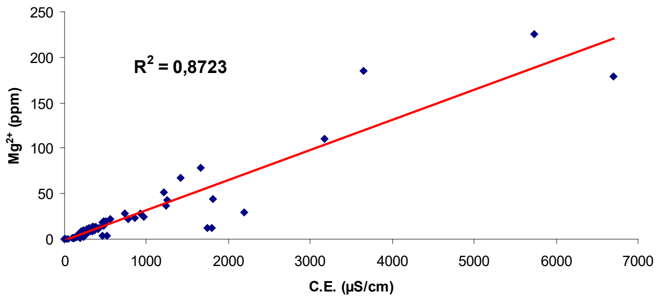

Fig. 5. *Correlation between the electrical conductivity and magnesium*

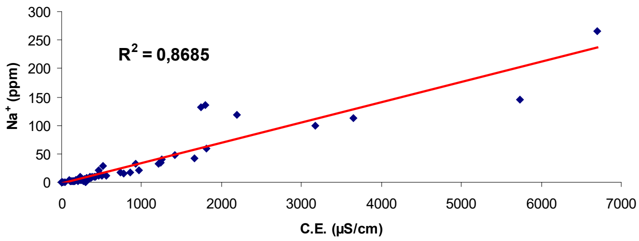

Fig. 6. *Correlation between the electrical conductivity and sodium*

Moreover, we can show that the electrical conductivity correlations with the anions presented a heterogeneous behavior. This correlation was excellent with NO_3^- (Fig. 7), but less so for either SO_4^{2-} or Cl^-, as could be expected (Fig. 8 and 9). This may be due to greater mobility and concentration of the NO_3^- anion. The resulting nitrate values in the first irrigation applications were very high and so they washed out quickly. In the case of the chlorides, the concentrations were lower and, possibly, the analytical method used (volumetric) was not the most appropriate because it brought a greater error than other analytical techniques.

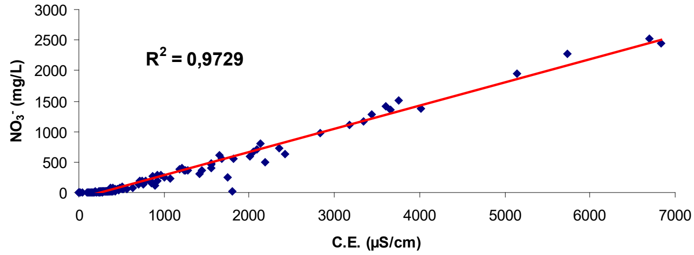

Fig. 7. *Correlation between the electrical conductivity and nitrates*

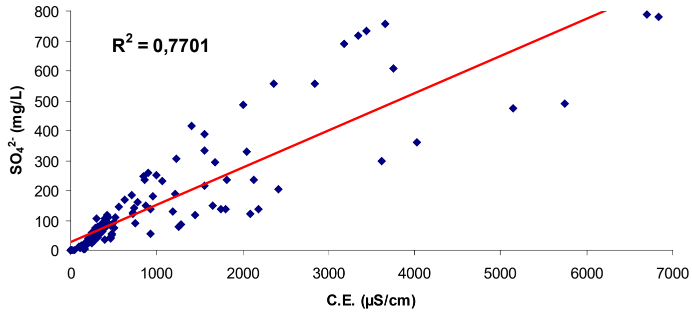

Fig. 8. *Correlation between the electrical conductivity and sulfates*

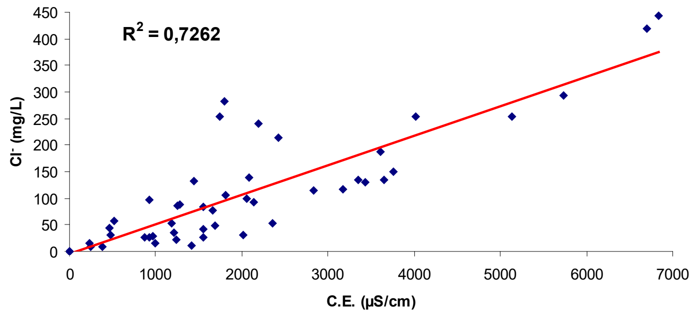

Fig. 9. *Correlation between the electrical conductivity and chlorides*

Sulfates are salts that have a lower solubility than halite. There were significant correlations between the SO_4^{2-} anion and the Mg^{2+}, Ca^{2+}, and K^+ cations (Fig. 10, 11 and 12). The highest correlation was obtained with Mg^{2+} that comes mainly from the substratum formed by magnesium limestone and dolomite subjected to a crushing process in the quarry plant (Figure 10). This may be due to the epsomite ($MgSO_4 \cdot 7H_2O$) having a higher solubility than the anhydrite and gypsum ($CaSO_4$ and $CaSO_4 \cdot 2H_2O$, respectively).

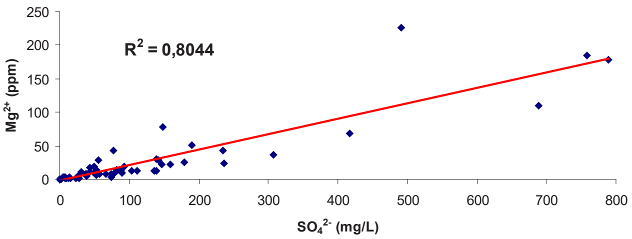

Fig. 10. *Correlation between the sulfates and magnesium*

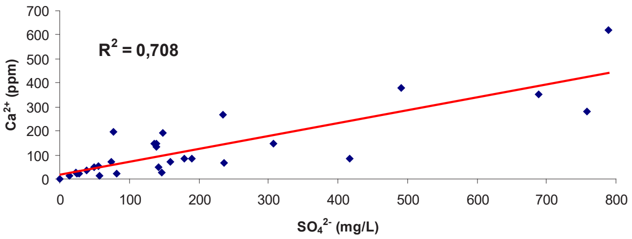

Fig. 11. *Correlation between the sulfates and calcium*

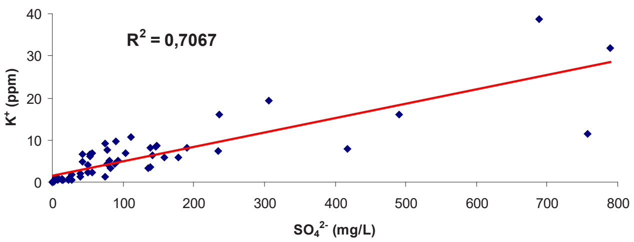

Fig. 12. *Correlation between the sulfates and potassium*

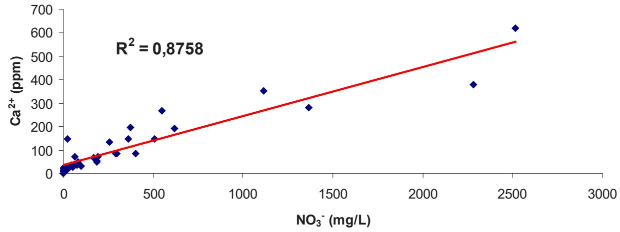

Fig. 14. *Correlation between the nitrates and calcium*

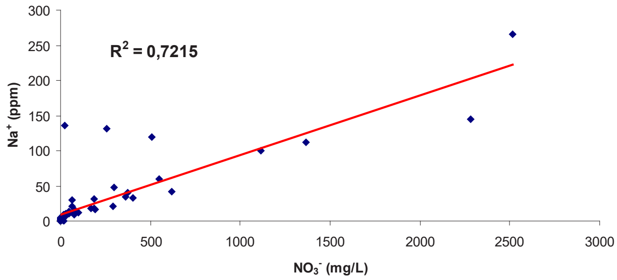

Fig. 15. *Correlation between the nitrates and sodium*

The good correlations obtained between the NO_3^- anion and the alkaline earth elements and the Na^+ were mainly due to their rapid percolation through the dissymmetrical columns, above all in the first irrigation applications (Fig. 13, 14 and 15).

Next, we will discuss the correlations obtained between the ions that formed very soluble salts (between 250 and 400 g/L). The only statistically significant correlation occurred with Na^+-Cl^- (Fig. 16). Predictably, the chlorides presented an excellent correlation with Na^+. NaCl (halite) is a very soluble salt and so geochemically it is very unstable and its mobility is very high.

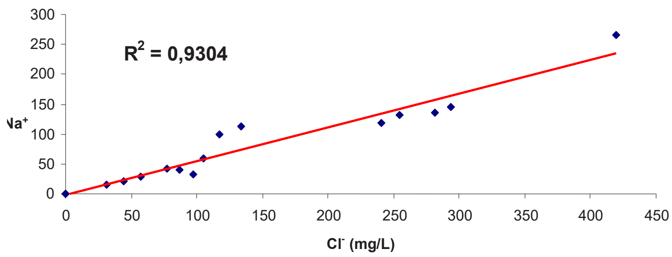

Fig. 16. *Correlation between the chlorides and sodium*

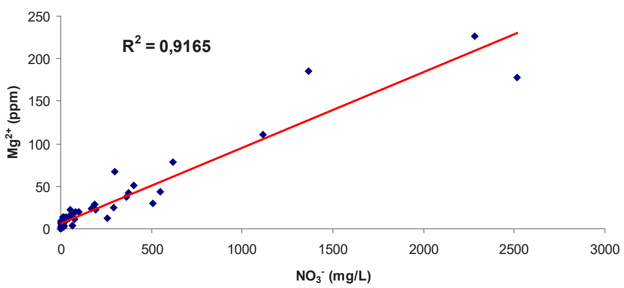

Fig. 13. *Correlation between the nitrates and magnesium*

4.1. Physical properties of the substratum

The experiment saw the bulk density decrease and the aggregate stability increase, thereby improving the structure.

4.2. Environmental risk

As for the environmental risk with respect to the contamination of aquifers in the sierras de Callosa and Vega Baja del Segura from wash water, we performed a comparison between the concentrations of the contaminants obtained in the leachates from our experiment and the established limit values for water of the third quality group of the Segura Hydrographic Confederation.

- The pH values were found to be within the limit value range (5.5-9).
- The electrical conductivity limit value is <1000 µS/cm (Jordán et al. 2008). These values will be met from the fourth irrigation application onward, while the values up to that point were far superior. However, the quality of the aquifer's groundwater is quite poor, reaching conductivities of 5000 µS/cm, and so this parameter, in principle, would not represent any environmental risk to the aquifer [5, 10, 24].
- The limit values for the chlorides (<700 mg/L), phosphates (<27 mg/L), and sulfates (<800 mg/L) were very superior to those obtained in all the irrigation applications.
- Significant nitrate concentrations appeared that may pose an environmental contamination risk.

4.3. Correlations between leachate parameters

- The electrical conductivity correlated well with the cations, with the exception of the potassium.
- Regarding the electrical conductivity correlations with the anions, they were found to be excellent in the case of nitrates, which may be due to their high concentration and solubility; however, as expected, they were not as much with the sulfates and chlorides.
- For sulfates, significant correlations were obtained with the Mg^{2+}, Ca^{2+}, and K^{+} cations, with the magnesium correlation highest, which could be due to it being more soluble [10].
- The good correlations between nitrates and the Ca^{2+}, Mg^{2+}, and Na^{+} cations could mainly be due to their high solubility, as they percolated rapidly in the first irrigation applications [10].
- The chlorides showed excellent correlation with the sodium. NaCl (halite) is very soluble and so its mobility is high [5, 10, 24].

References

[1] Jordán M.M., Mateu J., Boix A., A classification of sediment types based on statistical multivariate techniques. Water Air Soil Pollut., 107 (1998) 91-104.

[2] Tedesco M.J., Teixeira E.C., Medina C., Bugin A., Reclamation of spoil and refuse material produced by coal mining using bottom ash and lime. Environ Technol., 20(5) (1999) 523-529.

[3] Ram L.C., Srivasta N.K., Tripathi R.C., Jha S.K., Sinha A.K., Singh G., Manoharan V., Management of mine spoils for crop productivity with lignite fly ash and biological amendments. J Environ Manag 79(2) (2006) 73-187.

[4] Jordan M.M., Almendro M.B., Pina S., García-Orenes F., García-Sánchez E., Sabater M.C., Navarro J., Gómez I., Sewage sludge application for soil reclamation of limestone quarries. Test in columns using a calcareous mineral rejection. In: Water management and soil conservation in semi-arid environments, INRA, Marrakech, 2006.

[5] Jordán M.M., Pina S., García-Orenes, F., Almendro-Candel, M.B., García-Sánchez E., Environmental risk evaluation of the use of mine spoils and treated sewage sludge in the ecological restoration of limestone quarries. Environ Geol., 55 (2008) 453-462.

[6] FAO. In IUSS (Ed.), World Reference Base for Soil Resources. Rome: ISRIC, 2006.

[7] Novo L.A. B., Covelo, E.F., González, L., The potential of Salvia vernenaca for Phytoremediation of Copper Mine Tailing Amended with echnosol and compost. Water, Air and Soil Pollut., 224 (2013) 1513.

[8] Albiach R., Canet R., Pomares F., Ingelmo F., Organic matter components and aggregate stability after the application of different amendments to a horticultural soil. Bioresour Technol 76 (2001) 125–129.
[9] Pond A.P., White S.A., Milczarek M., Thompson T.L. Accelerated weathering of biosolid-amended copper mine tailings. J Environ Qual 34(4) (2005) 1293-1301.
[10] Jordán, M.M., García-Sánchez, E., Almendro-Candel. M.B., Pardo, F., Vicente, A.B., Sanfeliu, T., Bech J., Tenchnosols designed for rehabilitation of mining activities using mine spoils and biosolids. Ion mobility and correlations using percolation columns. Catena, 148 (2017) 74-80.
[11] Alcañiz, J.M., Comellas, I., Pujola, M., Sewage Sludge Restoration Handbook: Recovery of Marginal Lands. Ed. Junta de Sanejament, Generalitat de Catalunya, Barcelona, 1997.
[12] Sánchez-Andréu J., Jordá J.D., Juárez M., Mataix J., Dosing of iron chelates in limestone soils, in: Current problem in the use of fertilizars (1986) 228-232.
[13] Juárez M., Sánchez-Andréu J., Mataix J., Agricultural interest in sewage sludge treatment plant. Anal. Edafol. Agrobiol., 46(1-2) (1987) 211-228.
[14] Moreno Sánchez J.I., Hernández Fernández M.T., Costa Yagüe F., Characterization and fluctuation of physical and physical-chemical parameters in sewage Sludge, An. Edafol. Agrobiol., 45(5-6) (1986) 697-708.
[15] Hernández Fernández M.T., Moreno Sánchez J.Y., Costa Yagüe F., Characterization and fluctuation of carbon and nitrogen from sewage sludge. An. Edafol. Agrobiol., 45(5-6) (1986) 709-720.
[16] Giovannini G., Riffaldi R., Levi-Minzi R., Determination of organic matter in sewage Sludges, Soil Sci. Plant Anal. 16(7) (1985) 775-785.
[17] Cánovas, J., Agronomic quality of irrigation waters. Ed. Servicio de Extensión Agraria. Ministerio Agricultura, Pesca y Alimentación (M.A.P.A.), Madrid, 1980.
[18] Roldán A., García-Orenes F., Lax., A. An incubation experiment to determinate factors involving aggregation changes in an arid soil receiving urban refuse. Soil Biol. Biochem. 26 (1994) 1699-1707.
[19] Ministerio de Agricultura, Pesca y Alimentación (MAPA), Analysis Methods. Volumen III. Ed. Secretaría General Técnica, Madrid, 1986.
[20] Rodier J., Water Analysis. Análisis de las Aguas. Ed. Omega S.A., Barcelona, 1981.
[21] Sempere A., Oliver J., Ramos C., Simple determination of nitrate in soils by second-derivative spectroscopy. J. Soil Sci. 44 (1993) 633-639.
[22] Clapp, C.E., Stark S.A., Clay D.E., Larson W.E., Sewage sludge organic matter and soil properties. The role of organic matter in modern agriculture, chap. 10. Ed. Martinus Nijhoff Publishers, Dordrecht (Holland), 1986.
[23] USDA, Criteria for the evaluation of soils environmental quality, Manual of Soil Sciences. Technical report, 1999.
[24] Jordán M.M., Mateu J., Juan P., Navarro J., García E., Spatial dynamics of soil salinity under arid and semiarid conditions: geological and environmental implications. Environ Geol., 45(4) (2004) 448-456.