Risk areas in the application of sewage sludge on degraded soils in the province of Alicante (Spain)

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Abstract

Restoration of degraded soils with organic wastes could be a feasible practice to minimise erosion in the Mediterranean area, but this practice shows a risk of soil and groundwater pollution. Currently the use of sewage sludge to improve the nutrient contents of a soil is a common practice. The soil leaching in which a great amount of fertilizers is usually applied, favours the solubilization of inorganic compounds. In order to study the mobility of some of these elements through the soil, we have designed an experiment that tries to reproduce the behaviour of different compounds and heavy metals in the soil as a part of the non-saturated zone. A controlled experiment in a greenhouse using soil columns was used. A calcareous soil from the south-east of Spain was amended with 30000, 90000 and 180000 kg sludge/ha. Nitrate, nitrite, cadmium, and nickel were analyzed in soil samples at intervals of 15 cm of depth, during four months; also leachates were collected at the bottom of the columns and metals and nitrogen forms were thus analyzed. Total, available, exchangeable and soluble forms of these heavy metals were analyzed. We found high concentrations of nitrates and nitrites in leachates, which imply an important environmental risk. No important displacements of polluting metals were found along the soil profile.

Keywords: degraded soils, sewage sludge, nitrate, heavy metals mobility.

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1 Introduction

Many anthropic activities cause severe disturbances on the environment. Soils are one of the most affected environment pool. Soils in Mediterranean areas present low resilience to the different disturbances. Soil damage frequently leads to ecosystem degradation. Incorrect agricultural practices cause the abandonment of agricultural lands after soil impoverishment. Moreover, natural perturbations such as long-term drought in areas with overgrazing start erosion processes.

The degree of soils pollution caused by heavy metals depends on the capacity of the soil to immobilize and exchange metals, especially dependent on physico-chemical properties (mineralogy, grain size, organic matter), affecting soil particle surfaces and also on the chemical properties of the metal. These metals may be retained by soil components in the soil horizons near the surface, or may either precipitate or coprecipitate as sulphides, carbonates, oxides or hydroxides with Fe, Mn and Ca. In arid zones, carbonate effectively immobilizes heavy metals by providing an adsorbing or nucleating surface, and by buffering pH at values at which metals hydrolyze and precipitate. The mobility of trace metals reflects their capacity to pass through one soil compartment into another where the element is bound less energetically, the ultimate compartment being the soil solution which determines the bioavailability. The application of sludge to the land include the potential for applying too much or too little quantities of each nutrient; the presence of toxic constituents; and the possible detrimental effects on water quality from leaching, erosion, or runoff losses. Because of these potential problems, restrictions have been imposed on land application of sludge. The soil pollution and the groundwater quality decreasing due to the potentially toxic metals or nitrogen compounds are often assessed in terms of total concentrations. However, many forms of metals are intensely held in the soil and generally become immobile, although several factors (change in pH or redox conditions, soluble organic complexing agents, etc) may mobilize such forms [1, 2, 3].

2 Materials and methods

The experiment was carried out under controlled conditions inside a greenhouse (temperature around 20ºC and 50% of relative humidity). The procedure was based on the construction of 48 columns with a height of 60 cm, from a PVC pipe with an internal diameter of 10.5 cm. Each column was cut into four sections: 0-15, 15-30, 30-45 and 45-60 cm. These sections allowed us to study the differential mobility of Cd, Ni, NO_3^- and NO_2^- through the soil horizons. Similar experiments have been developed with columns of the same material [4], in order to evaluate the potential movement of Fe, Mn, Cu and Zn in sewage sludge-treated soils [5].

As specified in table 1, three treatments and one control treatment were made, according to the sludge quantity applied. The sludge was applied on the surface and mixed up with the soil simulating plow action, obtaining an homogeneous mixture of the sludge with the first 15 cm of the soil. Emmerich et al. [4, 6] also

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applied sludge in the first 15 cm of soil, in their studies on the movement of heavy metals in soils treated with sludge, and on the forms of heavy metal in the soil solution. This mixture was placed on the upper part of the column, (0-15 cm) having 12 columns per treatment.

The soil used for this experiment corresponds to a non-cultivated soil. It is an Antrosol, a young soil, modified by man's action. The calcium carbonate equivalent is high (68%), frequent in the soils of Southeastern Spain (table 2).

The sludge used in this experiment was from a waste water treatment plant, whose characteristics are shown in table 3.

Table 1: Sludge applied in each treatment.

Sludge (kg/ha)	Denomination
0	O
30000	L
90000	M
180000	H

Table 2: Characteristics of soil [7].

Parameter		Value	Parameter		Value
Clay loam texture			Munsell colour		
Sand 20<∅<2000μm	%	26	Dry	white	10YR 8/1
Silt 2<∅<20μm	%	34	Wet	lightly grey	10YR 7/2
Clay ∅<2μm	%	40	Total elements		
pH		8.66	Al	g/kg	18.556
E.C.	μS/cm	79.7	B	mg/kg	49.1
Active lime	%	19.8	Ba	mg/kg	59.6
$CaCO_3$ equival.	%	68	Be	μg/kg	500
Oxid. C	g/kg	2.0	Ca	g/kg	236.3
Oxidizable O.M.	g/kg	3.5	Cd	μg/kg	385
N Kjeldhal	g/kg	0.4	Cr	mg/kg	21.2
P available			Cu	mg/kg	9.7
$P_{\text{Burriel-Hernando}}$	mg/kg	15.67	Fe	g/kg	9.997
Ammonium acetate extraction			K	g/kg	3.188
Ca	g/kg	5.340	Li	mg/kg	9.7
K	g/kg	0.155	Mg	g/kg	4.552
Mg	g/kg	0.258	Mn	mg/kg	137.2
Na	g/kg	0.070	Mo	mg/kg	2.0
DTPA extraction			Na	g/kg	0.395
Cu	mg/kg	0.40	Ni	mg/kg	18.2
Fe	mg/kg	0.50	P	mg/kg	96.5
Mn	mg/kg	1.00	Sr	mg/kg	404.4
Zn	mg/kg	0.18	Zn	mg/kg	36.2

Table 3: Composition of sewage sludge (dry matter) [7].

Parameter		Value	C.I.	Parameter		Value	C.I.
Humidity.	%	82	3	Oxid. C.	%	19.7	2.8
T.O.M. $_{500°C}$	%	59.8	3.9	Oxid. O.M	%	33.9	4.8
Al	g/kg	11.33	1.18	Mg	g/kg	4.79	0.30
As	mg/kg	1.0	0.4	Mn	mg/kg	163	10
B	mg/kg	83	12	Mo	mg/kg	7	1
Ba	mg/kg	529	28	N	g/kg	41.17	1.07
Ca	g/kg	55.72	2.89	Na	g/kg	9.55	1.30
Cd	mg/kg	41.1	0.6	Ni	mg/kg	290	55
Cr	mg/kg	49	7	P	mg/kg	2375	256
Cu	mg/kg	411	48	Pb	mg/kg	101	6
Fe	g/kg	34.35	1.45	Sr	mg/kg	463	36
Hg	µg/kg	14	2	Ti	mg/kg	23	7
K	g/kg	1.37	0.14	V	mg/kg	96	12
Li	mg/kg	2.7	0.4	Zn	mg/kg	2261	126

In order to establish as much similarity as possible between real conditions and the experiment, the soils in the columns were irrigated with 100 mm of water every week. Four samples of soil were taken during the experiment with an interval of one month between each. Three columns were chosen per treatment, that is to say, 12 columns altogether separated in to the different layers. In each of them, nitrate, nitrite and total, exchangeable, available, and soluble Cd, and Ni were analyzed.

The analysis of nitrates was carried out using the method proposed by Sempere *et al* [8]. This analysis method eliminates the interference due to the presence of organic matter in the extract of the soil [9]. The determination of nitrites was carried out for colorimetric methodology using sulphanilamide and N-(1-Naphthyl)Ethylenediamine Dihydrochloride. The determination of total elements was carried out after microwave digestion of the samples using HNO_3 and H_2O_2 (4:1 v/v). In order to estimate the exchangeable elements, an ammonium acetate solution was used (1N, pH 7) [10]. Available metal for plants were determined by DTPA extraction following the Lindsay and Norvell method [11]. Soluble elements were determined after extraction with deionized water. (1:5 w/v). Cd and Ni in the different extracts and leachates were determined by atomic absorption spectrophotometry with a graphite furnace (GF). Total and available Ni were determined by flame atomic absorption spectrophotometry

3 Results and discussion

3.1 Nitrate

The content of nitrate increases with sludge application in every soil horizons, although the major content is located in the upper horizon (fig. 1). An important decrease of nitrate with depth has been observed, although it tends to increase in the last horizon (45-60 cm). This fact shows the facility of washing of this anion.

In the treatments, as a general rule, the content of nitrate decreases with time, though in the step between the second sampling and the third one, some case shows levels of nitrate that tend to be kept (H) or to increase (M), otherwise the control changes in a more irregular way, diminishing in the first two samplings, substantially increasing in the third one and diminishing again in the number 4. Harrach and Nemeth [12] think that the incorporation of sludge to the culture soils increases the level of NO_3^-.

3.2 Nitrite

In the first three samplings the content of nitrite increases with the treatment, not appearing this trend in the fourth sampling. The content of this anion increases with time in the first three samplings, diminishing in the last one, not existing in this one differences among the control and the different treatments with sewage sludge and among the horizons.

In all the treatments a major concentration of NO_2^- in the horizon 30-45 cm takes place. Rots can reach easily 30 cm, so that it would be suitable to consider this factor at the moment of applying sludge, together with the groundwater level (that would mark the limit that might reach the location of the nitrites in the soil).

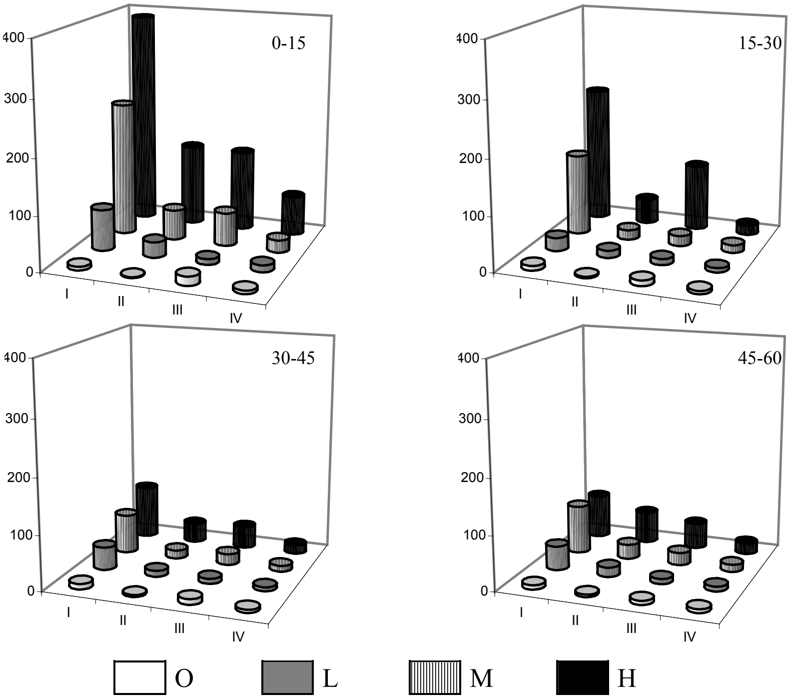

Figure 1: Nitrate content (mg/kg d.m.) in each horizon and treatment.

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3.3 Total amount of cadmium and nickel

Cadmium is in very low concentrations in the soil samples, and no evidence of a clear tendency to the increase of the concentration of this metal due to sludge presence was found. The contribution of Ni is more important. The increase of its concentration in the superficial horizons where organic fertilisation has been applied is the evidence of its important contribution. Excellent increases in depth are not observed, although horizon 15-30 is affected as therefore it is appraised in sampling 3 of the processing for the case of Ni.

3.4 Exchangeable cadmium and nickel

The cadmium content increases significantly with the processing in the first sampling in all the horizons (fig. 2). Its concentration is very low and at depth of 0-15 cm, certain relation with the sludge presence in the horizon is appraised. With regard to nickel significant increase with the processing in all the horizons is observed, especially in the upper ones. In the treated columns a tendency is appraised to diminish with time with the depth and. Only the nickel present in sludge seems to be the one that is extracted in greater amounts.

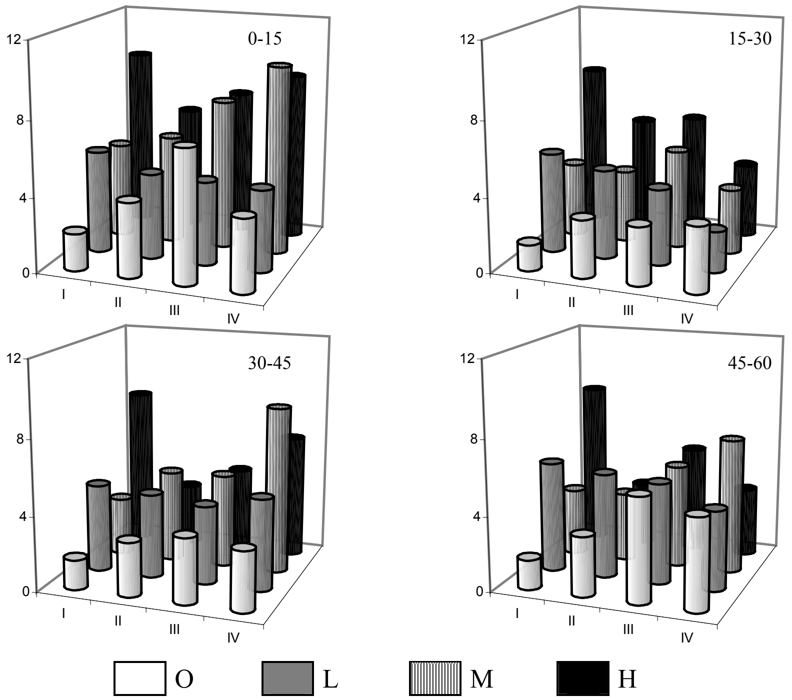

Figure 2: Exchangeable Cd content (μg/kg d.m.) in each horizon and treatment.

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3.5 Available cadmium and nickel

The extraction of Cd and Ni with DTPA leads to very low values, specially in the case of Cd. Without doubt it is important that the levels of available polluting agents are as low is possible in order to avoid their absorption in case the soil were cultivated. A significant increase of the cadmium concentration is observed with the processing in the superficial level, just like Hooda and Alloway found [13]. In the columns treated with sludge a diminution of the cadmium content is observed with depth (fig.3).

Nickel shows significant variations with the processing in the superior half of the column, remaining inferior half similar to the respective controls during the experiment. Nickel contents diminish with time. This fact implies either a greater retention of Ni by the components of the soil, or its loss by leaching, in a way that it should appear in the leachates.

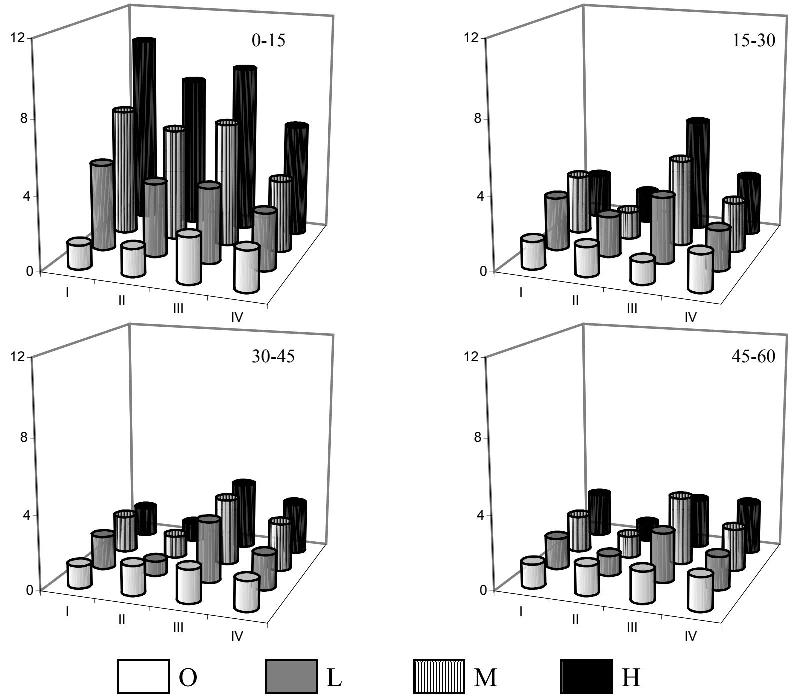

Figure 3: Available Cd content (μg/kg d.m.) in each horizon and treatment.

3.6 Soluble cadmium and nickel

In the first sampling, cadmium increases with sludge treatments in relation to the control in each depth, although it is not observed that it is directly proportional to the amount of sludge applied. There are no significant variations with depth. Generally the last samplings present smaller values than the first ones.

Nickel increases significantly in the surface level with treatments, but in a lesser extent in the 15-30 cm horizon (fig. 4). In the inferior half of the column there is no variation regarding the control. In the processing and samplings in which variations with depth are observed, these variations refer to a diminution. In the horizon 0-15 cm of the second sampling an important rise of nickel content takes place.

3.7 Cadmium and nickel in leachates

The concentrations of these polluting metals found in leachates are extremely low. Therefore, their mobility is not important in this limestone soil. Nickel increases with sludge application and diminishes with time, not existing differences between control and treatments in the last sampling (fig. 5). In this case a greater mobility of the metal is appraised initially in both proceedings.

Cadmium only increases with sludge in the third sampling (fig. 5). In the others samplings there are no significant differences between control and treatments. The presence of low molecular weight organic compounds, coming from the degradation of the organic matter in all the processing, from O to H treatment, can favour the displacement of Cd towards leachates.

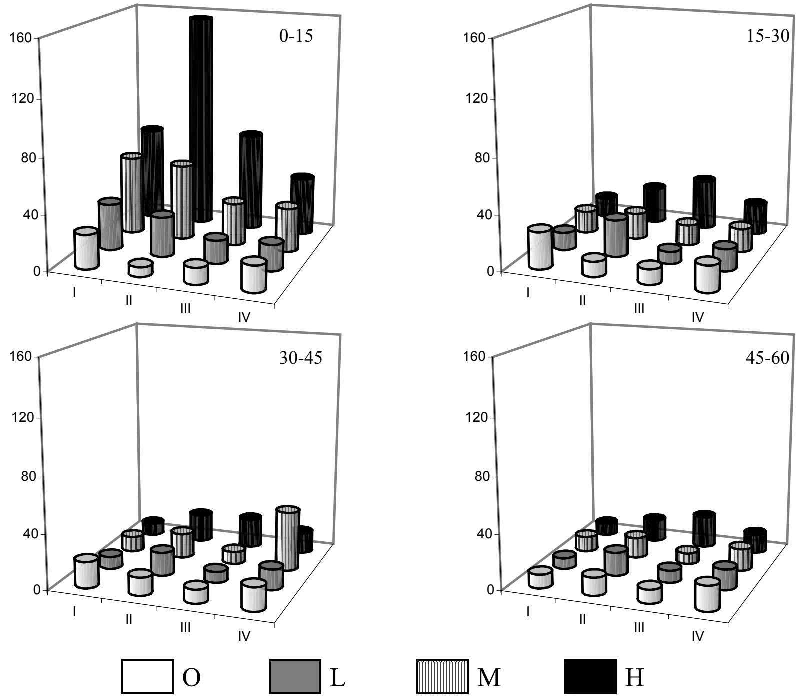

Figure 4: Soluble Ni content (µg/kg d.m.) in each horizon and treatment.

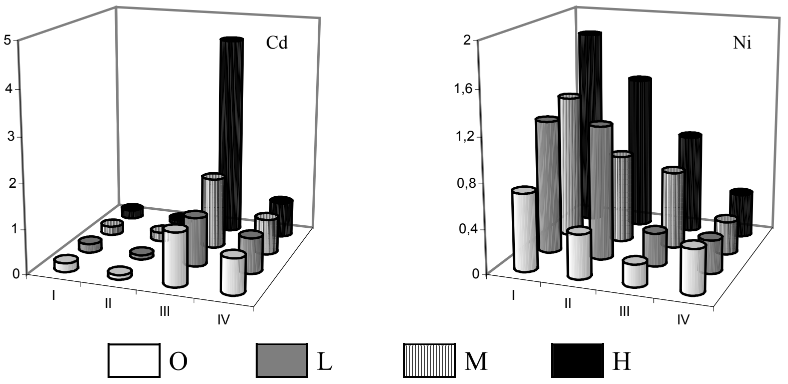

Figure 5: Cd and Ni content (µg/L) in leachates.

4 Conclusions

The application of sewage sludge to this Antrosol has a low risk of soil and groundwater pollution.

With regard to cadmium and nickel, (nickel being the one mainly available by plants), their presence in leachates has not been observed. This fact indicates that the polluting agents analysed in this research and under these conditions of irrigation do not have to mean a source of groundwater contamination.

This work and the accomplishment of similar experiments with other types of soils, could lead to the obtaining of more general conclusions and relations applicable to each concrete situation [14]. On the basis of this objective, we think that this work contributes data of interest and immediate application.

This is a starting point to develop a mathematical study that allows to model and to evaluate the evolution and mobility of these elements in calcareous and non-calcareous soils.

Acknowledgements

The authors would like to express their gratitude to BANCAJA and Universidad Miguel Hernández de Elche for the project "Áreas de riesgo en relación con la aplicación de lodos de depuradora en la provincia de Alicante. Aplicación de Sistemas de Información".

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