

## **SEWAGE SLUDGE APPLICATION FOR SOIL RECLAMATION OF LIMESTONE QUARRIES. TEST IN COLUMNS USING A CALCAREOUS MINERAL REJECTION**

**M.M. Jordán; M.B. Almendro-Candel; S. Pina; F. García-Orenes; E. García-Sánchez; M.C. Sabater; J. Navarro-Pedreño; I. Gómez-Lucas**  
*GEA- Grupo de Edafología Ambiental – Environmental Soil Science Group.  
Department of Agrochemistry and Environment. University Miguel Hernández,  
Avda. de la Universidad s/n. 03202, Elche, Alicante,  
SPAIN( [manuel.jordan@umh.es](mailto:manuel.jordan@umh.es))*

### **Résumé**

Un rejet minéral d'une carrière de pierre à chaux dans Cox, Alicante (le Sud-est de l'Espagne) a été amendé avec 3 et 9 kg boue d'épuration/m<sup>2</sup>. Le nitrate, l'ammonium, le cadmium et le nickel ont été analysés dans eaux de percolation rassemblé au fond des colonnes. Nous avons trouvé les hautes concentrations de nitrates et l'ammonium dans les eaux de percolation, qui implique un risque environnemental important. Nous suggérons que dans des environnements de la Méditerranée, la revégétation et l'irrigation qui peut être appliquée, soient particulièrement appropriés dans le début de la restauration du secteur dégradé et peuvent être faits avant les périodes d'averse en raison du risque des hautes pertes de nitrate. Le cadmium et la présence de nickel dans les eaux de percolation n'ont pas été importants dans cette expérience. Ce fait indique que les agents de pollution analysés dans ces colonnes avec un calcaire rejet minéral et dans ces conditions d'irrigation ne devraient pas être une source de pollution d'eau souterraine.

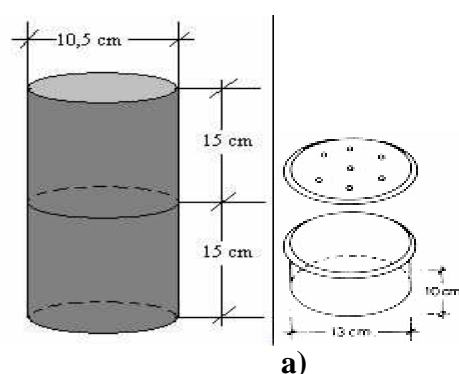
### **Introduction**

Soil is a major sink for heavy metals released into the environment. Many soils in industrialized countries are affected by acid deposition, mine waste and organic refuses, such as sewage sludge that introduce pollutants to the soil. The level of pollution of soils by heavy metals depends on the retention capacity of the soil, especially 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 near surface soil horizons or may 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 where metals hydrolyze and precipitate. The mobility of trace metals reflects their capacity to pass from one soil compartment to another where the element is bound less energetically, the ultimate compartment being soil solution which determines the bioavailability. Reclamation of limestone quarries working areas with organic wastes may be subjected to less restrictive regulations than the application of these materials in agriculture. Rejection materials coming from limestone quarries extraction are often used in the working reclamation process. These materials could be actually employed profitably once conveniently amended with organic matter. On the other hand, the amount of dehydrated sewage sludge that is subsequently composted or thermally dried is more and more important, but only a small proportion of it is used in agriculture.

New EC regulations could also difficult the use of this biosolid for agricultural purposes (Navarro-Pedreño et al, 2004).

## Materials and Methods

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 (Legret et al., 1988). A controlled experiment in a greenhouse using soil columns was used. The experiment was carried out under controlled conditions inside a greenhouse (20°C and 50% of relative humidity). The procedure was based on the construction of 36 columns with a height of 30 cm, from a PVC pipe with an internal diameter of 10.5 cm (Fig. 1). Each column was cut into two sections: 0-15 and 15-30 cm. In the case of limestone quarries, it may be possible to add higher dose of waste without causing environmental problems or food pollution. This type of application must be compatible with environmental security by avoiding displacement of dissolved pollutants to drainage. A mineral rejection from limestone outcrops was amended with 3 and 9 kg sludge/m<sup>2</sup>. The soils in the columns were irrigated with 100 mm of water every two weeks (Navarro-Pedreño et al, 2004). Nitrate, ammonium, cadmium, and nickel were analyzed in leachates collected at the bottom of the columns (Navarro-Pedreño et al, 2004). The analysis of nitrates was carried out using the method proposed by Sempere et al. (1993). This method eliminates the interference due to the presence of organic matter in the extract of the soil (Simal et al., 1985). The quantitative determination of the ammonium bases on the development of blue of indo-phenol for reaction of the ions ammonium treated with a dissolution of sodium hypochlorite and phenol. Cd and Ni in leachates were determined by atomic absorption spectrophotometry with graphite furnace (GF). Total and available Ni were determined by flame atomic absorption spectrophotometry.



**Figure 1.-** a) Columns with a height of 30 cm, from a PVC pipe with an internal diameter of 10.5 cm; b) Mineral rejection from the limestone quarry studied.

## Results and Discussion

Nitrates present high mobility being the most pollutant nitrogenous compounds. The tests carried out reveal a rapid wash of nitrates in the first irrigation (Bermond and Berzimed, 1991), diminishing in the third (table 1). Anion repulsion by the negatively charged mineral rejection surfaces will force nitrate into large pore centres, where the velocity is higher. This result could be used in an equation described by Gvirtman and Gorelick (1991) to estimate the transport velocity of NO<sub>3</sub><sup>-</sup> in this particular column system. Nevertheless, some of the parameters were not determined in this experiment. The percolation estimates, for instance, do not account for potential leaching by unsaturated flow. All the leaching was assumed to occur under saturated conditions. However, downward movement of water, along the nitrate, is possible, and probable, under unsaturated conditions. It was observed major concentrations of ammonium in the leachates porporcionally to major dose of sewage sludge applied. However, for low doses of sewage sludge a maximum concentration of NH<sub>4</sub><sup>+</sup> has been

detected in leachates proceeding from the second irrigation whereas for high doses of residue the maximum concentrations of  $\text{NH}_4^+$  were detected in the leachates of the third irrigation (table 2).

**Table 1.** Nitrate content (mg/L) in leachates for each irrigation and doses applied.

Sampling	$\text{NO}_3^-$ (mg/L)		
	Control	3 kg sludge/m <sup>2</sup>	9 kg sludge/m <sup>2</sup>
1	387.34	552.60	511.40
2	197.89	714.87	1850.43
3	58.16	182.28	428.42
4	17.05	28.65	34.05
5	9.06	9.55	16.05
6	6.05	6.87	8.69
7	5.69	5.72	7.63

Physical and chemical properties describe the system and provide an idea of possible nitrogen behaviour in the mineral rejection. The movement of ammonium and nitrate through the mineral rejection column at high values of pH and different doses of sewage sludge describes the behaviour of nitrogen in the field and can be used to predict N leaching from this substratum.

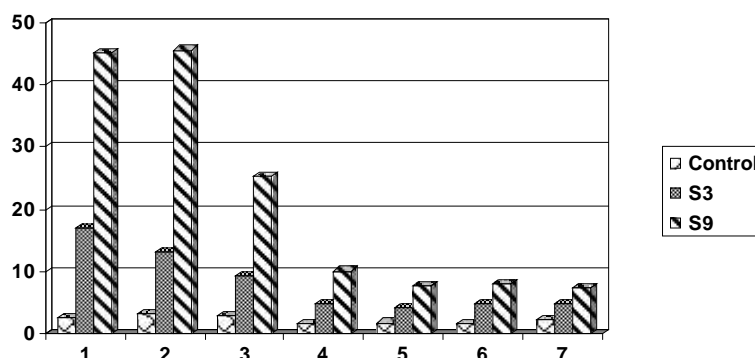
**Table 2.-** Ammonium content (mg/L) in leachates for each irrigation and doses applied.

Sampling	Control		3 kg sludge/m <sup>2</sup>		9 kg sludge/m <sup>2</sup>	
	Value	C.I.	Value	C.I.	Value	C.I.
1	33.63	0.35	262.87	2.47	549.43	7.68
2	0.12	0.05	0.79	0.18	0.14	0.03
3	0.03	0.00	0.26	0.09	0.70	0.11
4	0.01	0.00	0.52	0.04	0.50	0.04
5	0.02	0.00	0.21	0.01	0.28	0.01
6	0.04	0.02	0.07	0.01	0.06	0.00
7	0.04	0.01	0.14	0.05	0.08	0.01

C.I.: Confidence interval

This experiment demonstrated that this mineral rejection, under the conditions prevailing in this study, does not retain nitrate. Mineral rejection used has no nitrate adsorption capacity. Irrigation scheduling should be an important part of a management plan in limestone quarries reclamation. In the first sampling period (irrigation 1), carried out after the incorporation of the sewage sludge, a slight mobility of Cd was observed. In the second sampling, we observed again the low mobility (irrigation 2). This results could be interpreted by the fact that part of Cd should be still retained by the sewage sludge and part should have reacted with the mineral rejection remaining retained. In the third sampling (irrigation 3) we determined the major concentrations of Cd in the leachates. This third irrigation was the one that produces a real effect of mobilizing an important percentage of the retained Cd. Nevertheless, Ni presented a high mobility in this substratum from the beginning (Fig. 2), but due to its low concentration, it can be assured that risk of pollution was very poor. For these heavy metals, the concentrations found in leachates are extremely low, below the maximum level allowed in potable waters as EC regulations (Almendro et al., 2001). Performing a column study should provide enough information for the prediction of nitrate transport dynamics in a mineral rejection. This results, in a future research, could be incorporated into a model to predict  $\text{NO}_3^-$  leaching and its potential for groundwater contamination when developing a management plan for limestone quarries reclamation. The addition of sewage

sludge may be done according to the needs of the plant cover, reducing the surpluses of nitrogen of the soil able to be washed (Nogues et al., 2000).



**Figure 1.-** Evolution of Ni content ( g/L) in leachates after each irrigation and sewage sludge doses.

### Conclusions

We suggest that in Mediterranean environments, the revegetation and the irrigation that may be applied, is especially relevant in the beginning of the restoration of the degraded area and may be done before the rainfall periods due to the risk of high losses of nitrate. Cadmium and nickel presence in leachates has not been important in this experiment. This fact indicates that the polluting agents analysed in this columns with a calcareous mineral rejection and under these conditions of irrigation should not be a source of groundwater pollution. This work and the accomplishment of similar experiments with other types of soils, could lead to obtain more general conclusions and relations applicable to each concrete situation. On the basis of this objective, we think that this work contributes with 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 soils from these limestone quarries.

### Literature cited

Almendro Candel, M. B., Navarro Pedreño, J., Jordán Vidal, M. M., García Sánchez, E. y Mataix Solera, J., 2001. Ensayos de movilidad de compuestos nitrogenados en zona no saturada. In: Ballester, A.; Grima, J.; López, J.A.; Rodríguez, L. (eds.) Investigación, gestión y recuperación de acuíferos contaminados. Diputación de Alicante, Spain, pp. 23-34.

Bermond, A., Benzined, K., 1991. The localization of heavy metals in sewage treated soils; comparison of thermodynamics and experimental results. *Water, Air Soil Pollut.*, 57-58:883-890.

Gvirtzaman, H., Gorelick, S.M., 1991. Dispersion and advection in unsaturated porous media enhanced by anion exclusion. *Nature*, 352:793-795.

Legret M., Divet L., Juste C., 1988. Movement and speciation of heavy metals in a soil amended with sewage sludge containing large amount of Cd and Ni. *Wat Res* 22(8): 953-959.

Navarro-Pedreño, J., Almendro-Candel, M.B., Jordán, M.M., Mataix, J., García-Sánchez, E., 2004. Risk areas in the application of sewage sludge on degraded soils in Alicante province (Spain). *Geo-Environment*. WIT Press, Southampton, Boston, UK, pp 293-302.

Nogués, J., Herrero, J., Rodríguez-Ochoa, Boixadera, J., 2000. Land evaluation in a salt-affected irrigated district using an index of productive potential. *Env. Management*: 25 (2):143-152.

Sempere, A., Oliver, J., Ramos, C., 1993. Simple determination of nitrate in soils by second-derivative spectroscopy. *J. Soil Sci.*, 44. 633-639.

**Acknowledgements:** *The authors would like express our gratitude to Generalitat Valenciana for the financial support to the research project: GV/05/025.*