

## REMEDIATION OF Cd- AND Pb-POLLUTED SOIL BY TREATMENT WITH ORGANO-ZEOLITE CONDITIONER

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**Abstract**—The present work is part of a study focused on the use of organo-zeolite conditioner to remediate soil polluted by toxic elements. The Neapolitan yellow tuff (NYT) was utilized as a component of an organo-mineral sorbent/exchanger soil conditioner with pellet manure (NYT/PM) to reduce the mobility of Cd and Pb and recover plant performance in heavily polluted soils from illegal dumps near Santa Maria La Fossa (Lower Volturno river basin, Campania Region, southern Italy). Pot experiments were performed by adding the NYT/PM mixture (1:1, w/w) to polluted soil at the rates of 0%, 25%, 50% or 75% (w/w). Wheat (*Triticum aestivum*) was used as the test plant. The addition of organo-zeolite NYT/PM mixture significantly reduced the DTPA (diethylene-triamine-pentaacetic acid)-extractable Cd and Pb from 1.01 and 97.5 mg kg<sup>-1</sup> in the polluted soil, to 0.14 and 11.6 mg kg<sup>-1</sup>, respectively, in the soil amended with 75% NYT/PM. The best plant response was observed in amended soil systems treated with 25% NYT/PM, whereas larger additions induced plant toxicities due to increased soil salinity.

**Key Words**—Illegal Dumps, Ion Exchange, Natural Zeolites, Polluted Soils, Soil Remediation, Toxic Elements.

### INTRODUCTION

The presence in soil of large amounts of 'heavy metals', also defined as Potential Toxic Elements (PTE) (Alloway, 1990), is often connected to improper anthropogenic activities, such as uncontrolled industrial emissions or the illegal disposal of toxic waste. Concerns about the spread of land degradation have led to the enactment of a general policy for the management of contaminated sites (Prokop *et al.*, 2002). According to the new laws, polluted soils must be remediated and restored to their original agronomic and environmental functions. A possible way to recover polluted soils is to dilute the soil PTE concentration by adding a soil 'pedo-compatible' conditioner, which restricts PTE mobility via sorption-exchange mechanisms. Here we define pedo-compatible as any natural material or anthropogenic by-product that is analogous to a pedogenic substrate in a given environment and is susceptible to pedogenic processes, thereby evolving towards a stable and fertile soil. Natural zeolites (NZ) may qualify as pedo-compatible conditioners. In fact, natural zeolites exhibit distinctive cation exchange and adsorption properties (Colella, 1999a), as a result of high surface activity and their ability to take up some toxic

elements effectively (Colella, 1996; Pansini, 1996). Furthermore, natural zeolites also occur in soils that have developed on volcanic parent materials (Ming and Dixon, 1988; Scarpati *et al.*, 1993; de' Gennaro *et al.*, 2000; Hall, 2000).

There are a few encouraging studies that describe the possible large-scale application of NZ, either alone or in combination with organic amendments, for the recovery of degraded or polluted soils (Allen and Ming, 1995; Buondonno *et al.*, 2000a; Leggo and Ledésert, 2001; Coppola *et al.*, 2002; Mumpton, 2000).

The objective of this study was to evaluate the suitability of zeolitized tuff/organic matter mixtures as an organo-mineral sorbent/exchanger to recover degraded soils, with special reference to soil polluted by PTE. A previous investigation (Coppola *et al.*, 2002) focused on soils polluted by illegal disposal of toxic-noxious wastes in various unauthorized dump sites of the Lower Volturno river Basin (Campania region, south Italy). Results from laboratory experiments showed that treatments with a mixture of Neapolitan Yellow Tuff and pellet manure (NYT/PM) substantially reduce the DTPA-extractable Cd and Pb contents of soil, thus suggesting a restriction of PTE mobility in the soil/plant system. This paper deals with the effect of NYT/PM additions on Cd and Pb availability in soil, as well as on soil nutrients balance and plant growth in a pot experiment with wheat (*Triticum aestivum*).

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## MATERIALS AND METHODS

*Study area and toxic waste*

The Lower Volturno river Basin is situated in the Campanian Plain, and it is bounded by the Tyrrhenian Sea to the West, by Mount Massico and Roccamonfina Volcano to the North, by Mount Maggiore and the Tifatini chain to the East, and by the Phlegraean Fields to the South. The area, covering ~60,000 ha, represents some of the most valuable agricultural lands in southern Italy, used for the production of buffalo, fruit, tomatoes, tobacco, vegetables and cereals.

Illegal dumps have been discovered at various locations between the towns of Capua and Castelvoturno, not far from the left (southern) bank of the Volturno river (Figure 1), and placed under legal jurisdiction. The sizes of the contaminated sites vary widely from ~100 to 25,000 m<sup>2</sup>.

The toxic material deposited consisted of pellet foundry slags, containing considerable amounts of Cd and Pb (Table 1). The slags were alkaline, had high electrical conductivity, and consisted of particles with a diameter ( $\varnothing$ ) ranging from ~50 mm to <2 mm. The density of the material was 1.30–1.35 kg dm<sup>-3</sup> for particles with  $\varnothing$  <2 mm, and 2.57–2.62 kg dm<sup>-3</sup> for particles with  $\varnothing$  ranging from 2 to 16 mm.

*Soils*

The dominant soil in the investigated dump sites is a Vertic Xerofluvent, according to USDA Soil Taxonomy (USDA, 1999), with soil temperature, mineralogy and soil reaction classes corresponding to mesic, mixed and calcareous, respectively. Although the clay content is quite low (Table 2), the soil exhibits some vertic features such as cracks due to the presence of expansible clay minerals. The polluted soil chosen for the present investigation was sampled from the Ap surface horizon at 0–20 cm depth in an illegal dump area near Santa Maria La Fossa, not far from Capua, on the left side of the Volturno river (Figure 1). Reference samples were also sampled from uncontaminated neighboring soils.

Table 1. Main properties of pellet foundry slags (from Coppola *et al.*, 2002).

Feature	Mean	Min.	Max.
Total Cd (mg kg <sup>-1</sup> )	724	318	1305
Total Pb (mg kg <sup>-1</sup> )	32954	9937	59900
Extractable Cd* (mg kg <sup>-1</sup> )	83	36	164
Extractable Pb* (mg kg <sup>-1</sup> )	1211	48	3540
EC <sup>†</sup> (dS m <sup>-1</sup> )	17.2	1.9	38.6
pH <sup>†</sup>	10.2	9.9	10.7
Particle size (%)			
50 mm > $\varnothing$ >16 mm	4.7	4	6
16 mm > $\varnothing$ >2 mm	46.3	45	48
$\varnothing$ <2 mm	52.3	46	60

\* Extractable by DTPA; <sup>†</sup> Electrical conductivity (EC) and pH in material/water suspension 1:2.5 (w/v)

The soil properties were determined on the fine-earth fraction (<2 mm). Samples were air dried, crushed, and screened to pass a 2 mm sieve. The following analyses were carried out according to the Italian standard methods for soil analysis (MIPAF, 2000): carbonate content was determined with a Dietrich-Frühling calcimeter; soil pH and electrical conductivity (EC) were determined in 1:2.5 (w/v) soil/water suspension; organic carbon (OC) content was determined by the Walkley-Black method; particle-size analysis was performed by a sedimentation procedure; and the cation exchange capacity (CEC) was measured by the BaCl<sub>2</sub>-triethanolamine (TEA) method.

The following plant-available elements were extracted: Cd and Pb by DTPA; Na, K, Ca, Mg and P by Mehlich No 3 reactant (M3) (Mehlich, 1984); N-ammonium and N-nitrate by 2 N KCl. Total Cd and Pb were extracted by HCl/HNO<sub>3</sub> 3:1 (v/v). The Na and K were determined by emission spectrophotometry, Cd, Pb, Ca and Mg by atomic absorption spectrophotometry, and P, N-ammonium and N-nitrate by optical spectrophotometry. The main properties of a representative reference soil and of the polluted soil are reported in Table 2.

Table 2. Properties of the investigated soils.

	Reference soil	Polluted soil
Sand (2 mm > $\varnothing$ > 50 $\mu$ m; g kg <sup>-1</sup> )	420	327
Silt (50 $\mu$ m > $\varnothing$ > 2 $\mu$ m; g kg <sup>-1</sup> )	375	416
Clay ( $\varnothing$ < 2 $\mu$ m; g kg <sup>-1</sup> )	205	257
OC (g kg <sup>-1</sup> )	6.2	6.0
N (g kg <sup>-1</sup> )	0.7	0.5
C/N	8.6	11.5
pH-H <sub>2</sub> O	8.3	8.2
CEC (meq g <sup>-1</sup> )	0.213	0.221
CaCO <sub>3</sub> (g kg <sup>-1</sup> )	101	68
Total Cd (mg kg <sup>-1</sup> )	2.7	4.2
Total Pb (mg kg <sup>-1</sup> )	42.0	220.0
DTPA-Cd (mg kg <sup>-1</sup> )	0.1	1.0
DTPA-Pb (mg kg <sup>-1</sup> )	8.7	97.5



Figure 1. Illegal dump locations in the study area.

#### Organo-zeolite mineral sorbent/exchanger conditioner

The starting materials for the preparation of the organo-mineral sorbent/exchanger conditioner were as follows:

(1) Neapolitan yellow tuff (NYT), from Marano, (Napoli). This material represents the more recent (12,000 y. b.p.) tuffaceous formation of the Phlegraean Fields (Napoli, Italy), covering an area of  $\sim 13 \text{ km}^2$  (de' Gennaro and Langella, 1996). The NYT sample used for the present investigation, with the following chemical composition ( $\text{g kg}^{-1}$ ):  $\text{SiO}_2 = 529.1$ ,  $\text{Al}_2\text{O}_3 = 147.3$ ,  $\text{Fe}_2\text{O}_3 = 40.3$ ,  $\text{MgO} = 10.8$ ,  $\text{CaO} = 20.7$ ,  $\text{K}_2\text{O} = 75.7$ ,  $\text{Na}_2\text{O} = 27.6$ ,  $\text{P}_2\text{O}_5 = 1.1$ ,  $\text{H}_2\text{O} = 141.0$  (Buondomno *et al.*, 2000a), has a CEC, measured by the cross-exchange method (Colella *et al.*, 1982-83), of  $1.90 \text{ meq g}^{-1}$  and a zeolite content, estimated by the vapor desorption procedure (de' Gennaro and Colella, 1989), of 54%, with phillipsite = 37% and chabazite = 17%. Ancillary phases present in the tuff include analcime, K-feldspar, pyroxene, and a trace of mica. Note that although analcime is a zeolite, it does not take part in cation exchange to a great extent because its exchange kinetics are very slow at room temperature (Barrer and Hinds, 1953).

(2) Pellet manure (PM) ( $\text{C} = 275.0 \text{ g kg}^{-1}$ ;  $\text{N} = 46.5 \text{ g kg}^{-1}$ ;  $\text{pH} = 7.2$ ;  $\text{EC} = 17.130 \text{ dS m}^{-1}$ ; water content =  $192.0 \text{ g kg}^{-1}$ ), produced by SCAM Company, Modena.

Because the PM was a partially desiccated manure, the organo-zeolite mineral NYT/PM conditioner in our experiments was prepared by thoroughly mixing NYT and PM at a one to one ratio by weight.

#### Preparation of amended soil models (AM) and design of laboratory experiments

Four amended soil models (AM) were prepared by adding the NYT/PM conditioner to polluted soil samples at a rate of 0, 25, 50 and 75 wt.% conditioner (Coppola *et al.*, 2002); these are referred to as AM-0, AM-25, AM-50 and AM-75, respectively. 3000 g of each AM were placed into 4 liter pots, sowed with wheat (*Triticum aestivum* at a rate of 25 seeds per pot), and watered

weekly at field capacity. Pots with reference soil (RS) without any treatment were also prepared. Neither AM nor RS pots were supplied with fertilizers.

In consideration of the low plant mass produced in the pot experiment, the whole shoots were harvested after 90 days, carefully washed, dried at  $80^\circ\text{C}$ , ground and digested by  $\text{HNO}_3/\text{HClO}_4$  (Mills and Jones, 1996), and then analyzed for Cd and Pb. Plants grown in the RS pots were considered as a reference standard. All the soil was collected from each AM and RS pot, air dried, crushed and sieved to 2 mm, and then analyzed as previously described. Three replicates of each AM and RS were prepared. Data were expressed on a dry-weight ( $105^\circ\text{C}$ ) basis.

## RESULTS AND DISCUSSION

The total Cd and Pb contents averaged 2.7 and 42.0 mg per kg of soil, respectively, in the reference soil, whereas the polluted soil samples contained average total Cd and Pb contents as large as 4.2 and  $220 \text{ mg kg}^{-1}$ , respectively (Table 2). These values agree with literature data for Cd and Pb concentrations in agricultural or polluted soils (Alloway, 1990; Kabata-Pendias and Pendias, 1992; Pais and Jones, 1997). With reference to available Cd and Pb forms, 0.1 mg DTPA-Cd and 8.7 mg DTPA-Pb were found per kg of reference soil, whereas DTPA-Cd and DTPA-Pb amounts in the polluted soil increased to 1.01 and  $97.5 \text{ mg kg}^{-1}$ , respectively (Table 2).

The addition of the organo-zeolite NYT/PM mixture effectively reduced the DTPA-extractable Cd and Pb level of the investigated polluted soil. The DTPA-Cd content decreased from 1.01 in the AM-0 sample to  $0.14 \text{ mg kg}^{-1}$  in the AM-75 sample (Figure 2), and the DTPA-Pb content decreased from 97.5 in the AM-0 sample to  $11.6 \text{ mg kg}^{-1}$  in the AM-75 sample (Figure 3). Therefore, when the NYT/PM conditioner was added to the polluted soil at a rate of 75%, the availability of Cd and Pb decreased to levels corresponding to the respective amounts observed in the non-

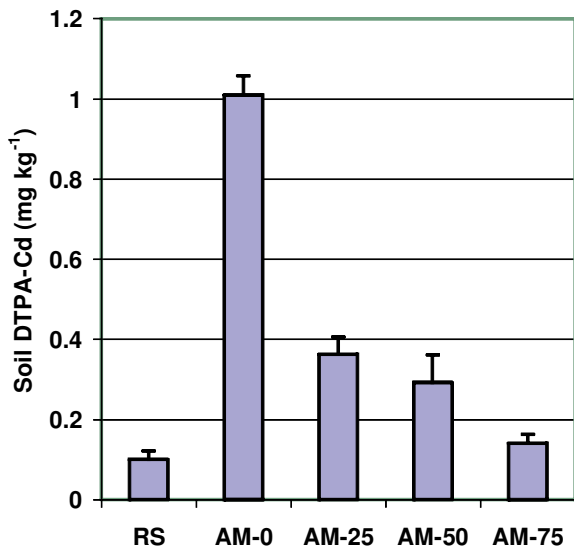


Figure 2. Distribution of DTPA-Cd in the reference soil (RS) and in the different amended soil models (AM). Bars on histograms indicate standard errors.

polluted reference soil. On average, we estimate that a unitary addition of 1% NYT/PM to soil reduced the extractability of  $\sim 0.01 \text{ mg kg}^{-1}$  Cd and of  $\sim 1.15 \text{ mg kg}^{-1}$  Pb. Such differing effects of NYT/PM addition on Cd and Pb extractability is probably a result of their different interactions with the various components of the investigated systems, e.g. soil, zeolitized tuff and organic matrix. In fact, several factors and processes govern Cd and Pb mobility (Alloway, 1990; Kabata-Pendias and Pendias, 1992; Wiers *et al.*, 1982), such as: the nature and amount of the exchanger/sorbent; the specific affinity of each cation for selective exchange/sorption sites; the pH, composition and ionic strength of the soil solution; the relative stability of metal complexes with organic ligands; and the competition with other metal ions and the interaction with counter-anions. It is therefore difficult to estimate the prevailing influence of each of the above factors and processes on the final Cd and Pb budget. Additionally, the alkaline soil reaction could probably promote the precipitation of Cd and Pb as carbonates and/or hydroxides. Nevertheless it is undeniable that phillipsite and chabazite, present in the Neapolitan yellow tuff, may play a predominant role on the differential Cd and Pb mobility observed in the experimental systems, considering that both zeolites are much more selective for Pb than for Cd (Colella *et al.*, 2001; de' Gennaro *et al.*, 2002). In particular, the equilibrium constants,  $K_a$ , were found to be 22.8 and 4.1 for the Na/Pb pair in phillipsite and chabazite, respectively, and 0.025 and 0.57 for the Na/Cd pair in phillipsite and chabazite, respectively (Colella, 1999b). This is in large part connected to ion exchange by zeolites with the possible minor involvement of adsorption on the external surface of the microporous minerals (Misaelides *et al.*, 1994, 1995).

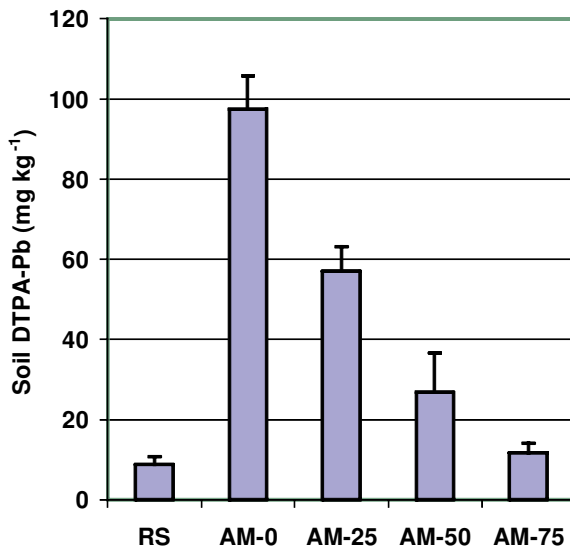


Figure 3. Distribution of DTPA-Pb in the reference soil (RS) and in the different amended soil models (AM). Bars on histograms indicate standard errors.

It is noteworthy that for both DTPA-Cd and DTPA-Pb, the reduction was much larger than that expected by simple soil dilution due to the different NYT/PM additions. In fact, the initial DTPA-Cd content was reduced to 64.4%, 71.3% and 86.1% after 25%, 50% and 75% NYT/PM addition rates, respectively, and the initial DTPA-Pb was reduced to 41.6%, 72.6% and 88.1%, respectively. This is probably due to effective sorption by the NYT/PM conditioner.

Figure 4 shows the dry matter (DM) of shoots harvested from pots containing the reference soil (RS) or the amended soil models (AM). For RS and AM-0

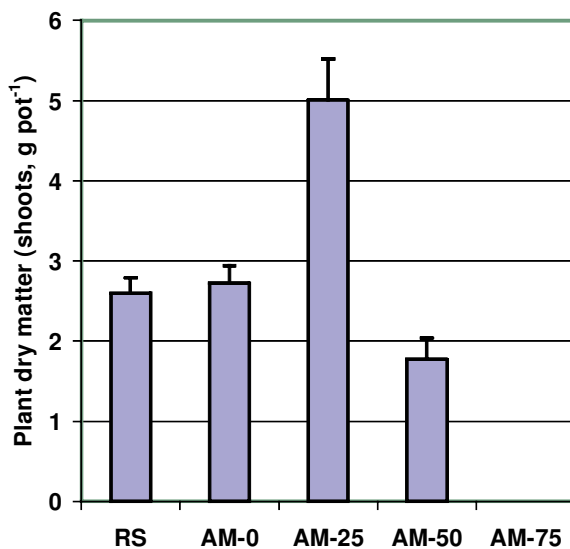


Figure 4. Wheat dry matter (shoots) in the reference soil (RS) and in the different amended soil models (AM). Bars on histograms indicate standard errors.

pots the DM was 2.6 and 2.7 g pot<sup>-1</sup>, respectively; in AM-25 the DM production significantly increased to 5.0 g pot<sup>-1</sup>, with a relative increase of +84%. This was probably due to the substantial amounts of plant nutrients supplied by the addition of the NYT/PM conditioner (Table 3). In contrast, DM strongly decreased in the AM-50 samples, and it was practically nil in the AM-75 samples, where no plant survived.

The reduction in plant productivity in the AM-50 and AM-75 samples may be explained by the increase of soil EC to 5.52 and 7.46 dS m<sup>-1</sup>, respectively, mainly due to the contribution of the pellet manure present in the organo-zeolite conditioner, which exhibited an EC of 17.130 dS m<sup>-1</sup>. The increase of soil salinity in the AM samples was clearly connected with a large and almost linear increase in extractable soil nutrients (Table 3) with special reference to K, Na, N-nitrate and P. Potassium and Na were probably provided by both NYT and PM (Buondonno *et al.*, 2000a) or by just NYT (Buondonno *et al.*, 2000b), but it was evident that P and N forms arose substantially from the degradation and evolution of PM (Buondonno *et al.*, 2000a).

It is well known that high concentrations of salts in soil solutions can adversely influence plant growth through direct osmotic effects, specific-ion effects, nutrients imbalance, as well as through changes in soil physical and chemical properties that can result in deterioration of crop production (Keren, 2000). Wheat is considered moderately tolerant of Na and of soil salinity, and values of electrical conductivity of 3–6 dS m<sup>-1</sup> in a water-saturated soil extract represents the limiting threshold for growth and productivity (Fageria *et al.*, 1991; Fageria, 1992; Keren, 2000). Considering that the

EC was measured in our experiments using 1:2.5 soil:water extracts, *i.e.* more dilute than water-saturated soil extracts, we can infer that the unfavorable plant conditions that occurred in the AM-50 and AM-75 samples were mainly caused by the detrimental effect of soil salinity, together with some Na toxicity. Treatment with NYT/PM conditioner also induced a moderate soil pH decline, which is interpreted as essentially due to manure transformation, although a zeolite contribution in determining pH cannot be excluded (Filippidis *et al.*, 1996; Charistos *et al.*, 1997).

Figure 5 shows the Pb uptake by shoots harvested from RS and AM pots. Literature data (Mengel and Kirkby, 1987; Kabata-Pendias and Pendias, 1992; Pais and Jones, 1997) indicate that plants can accumulate large amounts of Pb, especially in roots, without any visible effect on their appearance or yield. The background Pb content in plants growing in uncontaminated areas ranges from 0.1 to 10 mg kg<sup>-1</sup> on a dry-weight (DW) basis, whereas excessive Pb levels in plants from contaminated areas can be up to tens or hundreds of mg kg<sup>-1</sup>. Kabata-Pendias and Pendias (1992) report that Pb levels (DW basis) in forage plants average 2.1 mg kg<sup>-1</sup> for grasses, 2.5 mg kg<sup>-1</sup> for clovers, and 0.4–0.6 mg kg<sup>-1</sup> in wheat grains. More recently, Leggo and Ledéser (2001) found a concentration of 3 mg per kg in shoots of wheat (*Triticum aestivum*) grown on a toxic substrate containing 670 mg Pb per kg. In our experiment, the background level of Pb in shoots from non-polluted RS pots was 0.68 mg kg<sup>-1</sup>, which increased significantly to 1.24 mg kg<sup>-1</sup> in the polluted soil model AM-0 containing 220 mg Pb per kg soil. The NYT/PM treatment had a notable effect on the Pb content in plant

Table 3. Electrical conductivity (EC, dS m<sup>-1</sup>), pH, and available nutrients (mg kg<sup>-1</sup>) in reference soil (RS) and amended soil models (AM) (mean values with the respective standard errors in parentheses).

Parameter	RS	AM-0	AM-25	AM-50	AM-75
EC	0.18 (0.01)	0.23 (0.02)	3.44 (0.13)	5.52 (0.26)	7.46 (0.44)
pH	8.3 (0.08)	8.2 (0.01)	7.7 (0.03)	7.6 (0.03)	7.6 (0.03)
Na <sup>+</sup>	34.4 (0.9)	39.1 (2.7)	532.1 (30.9)	874.4 (22.6)	1234.7 (38.6)
K <sup>+</sup>	55.2 (3.3)	71.4 (1.9)	908.5 (30.9)	1800.2 (37.1)	2273.3 (106.6)
Ca <sup>2+</sup>	999.3 (19.5)	1030.7 (61.0)	1061.3 (84.5)	1308.7 (88.9)	1461.3 (62.4)
Mg <sup>2+</sup>	51.5 (0.5)	129.3 (4.9)	134.2 (4.6)	166.7 (5.8)	178.5 (3.7)
NH <sub>4</sub> <sup>+</sup>	28.2 (0.9)	31.1 (1.9)	102.6 (7.3)	134.3 (4.0)	262.6 (20.9)
NO <sub>3</sub> <sup>-</sup>	54.9 (2.0)	76.3 (5.4)	397.1 (68.3)	836.4 (9.0)	1299.6 (60.2)
P	2.1 (0.0)	1.5 (0.1)	42.3 (1.5)	82.4 (1.6)	111.7 (4.8)

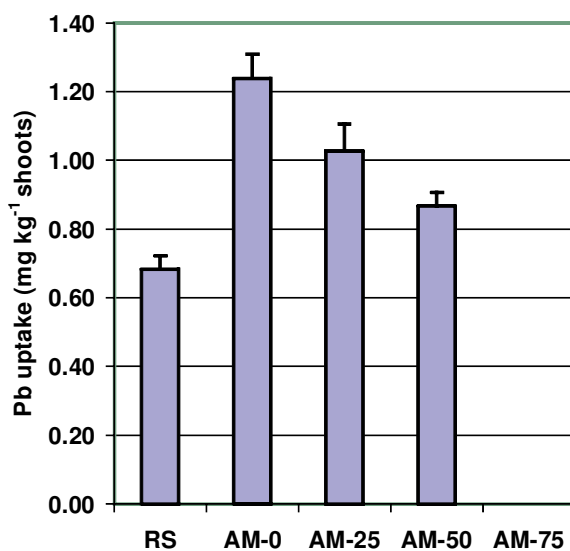


Figure 5. Pb uptake by wheat (shoots) in the reference soil (RS) and in the different amended soil models (AM). Bars on histograms indicate standard errors.



tissue, which decreased almost linearly to 1.03 mg kg<sup>-1</sup> for AM-25 and to 0.87 mg kg<sup>-1</sup> for AM-50.

In contrast to the results for Pb, the Cd content in shoots was very small and ranged from 0.06 to 0.08 mg kg<sup>-1</sup>, averaging 0.066 mg kg<sup>-1</sup>, with no significant differences among RS and AM pots. Thus, although different DTPA-Cd amounts were extracted chemically by the investigated soil samples, the Cd uptake and translocation in shoots was almost uniformly low. This is probably explained by the fact that Cd uptake by plants is at a maximum in acidic environments (pH = 4.5–5.5) and decreases drastically as the pH increases, with a minimum at the alkaline soil reaction (Mengel and Kirkby, 1987; Kabata-Pendias and Pendias, 1992; Pais and Jones, 1997). Furthermore, the presence of Ca strongly depresses Cd uptake (Mengel and Kirkby, 1987). In our RS and AM samples the pH was quite alkaline, ranging from 8.3 to not less than 7.6, and the M3-extractable Ca was very high, ranging from 999 to 1461 mg kg<sup>-1</sup>.

### CONCLUSION

Our experimental results are in agreement with literature data (Leggo and Ledésert, 2001; Coppola *et al.*, 2002) and confirm that an organo-mineral conditioner prepared as a mixture of Neapolitan Yellow Tuff and pellet manure is an active sorbent/exchanger system to amend soil polluted by Cd and Pb, with special reference to agricultural lands of high socio-economic value. The mobility of both toxic elements in soil was significantly reduced by amendment with the organo-zeolite conditioner, and plant performance partially recovered by the addition of 25 g NYT/PM per 100 g soil. However, addition rates of 50 g and 75 g per 100 g of polluted soil resulted in negative plant response due to soil salinity excess and toxicity. Hence, future research steps should focus on:

(1) testing of a larger number of organo-zeolite addition rates between 0 and 50%, in order to assess the optimal amendment treatment;

(2) testing of various organic matrix/zeolitic tuff ratios, in order to maximize the sorption-exchange activity, re-balance the nutrient availability, and minimize unwelcome side-effects such as soil salinity;

(3) comparison of natural zeolitic materials with different contents of phillipsite, chabazite and clinoptilolite, to evaluate the specific toxic ion selectivity and possible synergistic/antagonistic effects; and

(4) comparison of organic matrices from different sources to evaluate the specific susceptibility to the degradation and transformation.

### REFERENCES

Allen, E.R. and Ming, D.W. (1995) Recent progress in the use of natural zeolites in agronomy and horticulture. Pp. 477–490 in: *Natural Zeolites '93. Occurrence,*

*Properties, Use* (D.W. Ming and F.A. Mumpton, editors). International Committee on Natural Zeolites, Brockport, New York.

Alloway, B.J. (ed.) (1990) *Heavy Metals in Soils*, 2nd edition. Blackie Academic and Professional, Glasgow, UK, 368 pp.

Barrer, R.M. and Hinds, L. (1953) Ion-exchange in crystals of analcite and leucite. *Journal of the Chemical Society*, 1879–1888.

Buondonno, A., Coppola, E., Caianiello, A., Di Sarno, I., Langella, A. and Marino, R. (2000a) Short-term effects of Italian zeolitic tuffs on the availability of beneficial and toxic elements in soil. Pp. 459–470 in: *Natural Zeolites for the Third Millennium* (C. Colella and F.A. Mumpton, editors). E. De Frede Editore, Naples, Italy.

Buondonno, A., Colella, C., Coppola, E., de' Gennaro, M. and Langella, A. (2000b) Quantitative and kinetics of K and P release from Italian zeolitized tuffs. Pp. 449–458 in: *Natural Zeolites for the Third Millennium* (C. Colella and F.A. Mumpton, editors). A. De Frede Editore, Naples, Italy.

Charistos, D., Godelitsas, A., Tsiplis, C., Sofoniou, M., Dwyer, J., Manos, G., Filippidis, A. and Trintafyllidis, C. (1997) Interaction of natrolite and thomsonite intergrowth with aqueous solutions of different initial pH values at 25°C in the presence of KCl: Reaction mechanisms. *Applied Geochemistry*, **12**, 693–703.

Colella, C. (1996) Ion exchange equilibria in zeolite minerals. *Mineralium Deposita*, **31**, 554–562.

Colella, C. (1999a) Natural zeolites in environmentally friendly processes and applications. Pp. 641–655 in: *Porous Materials in Environmentally Friendly Processes* (I. Kiricsi, G. Pál-Borbély, J.B. Nagy and H.G. Karge, editors). Studies in Surface Science and Catalysis, No. **125**, Elsevier, Amsterdam, The Netherlands.

Colella, C. (1999b) Environmental applications of natural zeolitic materials based on their ion exchange properties. Pp. 207–224 in: *Natural Microporous Materials in the Environmental Technology* (P. Misaelides, F. Macasek, T.J. Pinnavaia and C. Colella, editors). NATO Sciences Series No. E **362** (Applied Sciences), Kluwer A.P., Dordrecht, The Netherlands.

Colella, C., de' Gennaro, M., Franco, E. and Aiello, R. (1982–83) Estimation of zeolite content in Neapolitan yellow tuff. 1. Phillipsite in nearly monozeolitic deposits. *Rendiconti Società Italiana Mineralogia e Petrologia*, **38**, 1423–1427.

Colella, C., Torracca, E., Colella, A., de Gennaro, B., Caputo, C., de' Gennaro, M. (2001) Ion-exchange features of intermediate-silica sedimentary phillipsite. In: *Zeolites and Mesoporous Materials at the Dawn of the 21st Century* (A. Galarneau, F. Di Renzo, F. Fajula, J. Vedin, editors). Studies in Surface Science and Catalysis, No. **135**, Elsevier, Amsterdam, The Netherlands. Paper 01-O-05 (CD ROM).

Coppola, E., Battaglia, G., Bucci, M., Ceglie, D., Colella, A., Langella, A., Buondonno, A. and Colella, C. (2002) Neapolitan yellow tuff for the recovery of soils polluted by potential toxic elements in illegal dumps of Campania Region. Pp. 1759–1766 in: *Impact of Zeolites and other Porous Materials on the New Technologies at the Beginning of the New Millennium* (R. Aiello, G. Giordano and F. Testa, editors). Studies in Surface Science and Catalysis, **142b**, Elsevier, Amsterdam, The Netherlands.

de Gennaro, B., Colella, A., Aprea, P. and Colella, C. (2002) Evaluation of intermediate-silica sedimentary chabazite as exchanger for radioactive cations. *Microporous and Mesoporous Materials*, **61**, 159–165.

de' Gennaro, M. and Colella, C. (1989) Use of thermal analysis for the evaluation of zeolite content in mixtures of hydrated phases. *Thermochimica Acta*, **154**, 345–353.

de' Gennaro, M. and Langella, A. (1996) Italian zeolitized rocks of technological interest. *Mineralium Deposita*, **31**,

- 452–472.
- de' Gennaro, M., Cappelletti, P., Langella, A., Perrotta, A. and Scarpati, C. (2000) Genesis of zeolites in the Neapolitan Yellow Tuff. Geological, volcanological and mineralogical evidence. *Contributions to Mineralogy and Petrology*, **139**, 17–35.
- Fageria, N.K. (1992) *Maximizing Crop Yields*. Marcel Dekker Inc. New York, USA, 274 pp.
- Fageria, N.K., Baligar, V.C. and Jones, C.A. (1991) *Growth and Mineral Nutrition of Field Crops*. Marcel Dekker Inc., New York, USA, 426 pp.
- Filippidis, A., Godelitsas, A., Charistos, D., Misaelides, P. and Kassoli-Fournaraki, A. (1996) The chemical behavior of natural zeolites in aqueous environments: Interactions between low-silica zeolites and 1 M NaCl solutions of different initial pH-values. *Applied Clay Science*, **11**, 199–209.
- Hall, A. (2000) Large eruptions and large zeolite deposits. Pp. 161–175 in: *Natural Zeolites for the Third Millennium* (C. Colella and F.A. Mumpton, editors). A. De Frede Editore, Naples, Italy.
- Kabata-Pendias, A. and Pendias, H. (1992) *Trace Elements in Soils and Plants*, 2nd edition, CRC Press, Boca Raton, Florida, USA, 365 pp.
- Keren, R. (2000) Salinity. Pp. G, 3–63 in: *Handbook of Soil Science*, (M.E. Sumner, editor). CRC Press, Boca Raton, Florida, USA.
- Leggo, P.J. and Ledésert, B. (2001) Use of organo-zeolitic fertilizer to sustain plant growth and stabilize metallurgical and mine-waste sites. *Mineralogical Magazine*, **65**, 563–570.
- M.I.P.A.F. (Ministero per le Politiche Agricole e Forestali – Osservatorio Nazionale Pedologico per la Qualità del Suolo) (2000) *Metodi di Analisi Chimica del Suolo*, No. 1124.2, FrancoAngeli Ed., Milano, Italy.
- Mehlich, A. (1984) Soil test extractant: a modification of the Mehlich 2 extractant. *Communications in Soil Science and Plant Analysis*, **15**, 1409–1416.
- Mengel, K. and Kirkby, E.A. (1987) *Principles of Plant Nutrition*, 4th edition. International Potash Institute, Bern, Switzerland, 687 pp.
- Mills, H.A. and Jones, J.B., Jr. (1996) *Plant Analysis Handbook II*. MicroMacro Publishing, Athens, Georgia, USA, 422 pp.
- Ming, D.W. and Dixon, J.B. (1988) Occurrence and weathering of zeolites in soil environments. Pp. 699–715 in: *Occurrence, Properties and Utilization of Natural Zeolites* (D. Kalló and H.S. Sherry, editors). Akadémiai Kiadó, Budapest, Hungary.
- Misaelides, P., Godelitsas, A., Charistos, V., Ioannou, D. and Charistos, D. (1994) Heavy metal uptake by zeolitic rocks from Metaxades, Thrace, Greece: an exploratory study. *Journal of Radioanalytical and Nuclear Chemistry*, **183**, 159–166.
- Misaelides, P., Godelitsas, A. and Filippidis, A. (1995) The use of zeoliferous rocks from Metaxades - Thrace, Greece, for the removal of cesium from aqueous solutions. *Fresenius Environmental Bulletin*, **4**, 227–231.
- Mumpton, F.A. (2000) Natural Zeolites: where have we been, where are we going? Pp. 19–34 in: *Natural Zeolites for the Third Millennium* (C. Colella and F.A. Mumpton, editors). A. De Frede Editore, Naples, Italy.
- Pais, I. and Jones, J.B. (1997) *The Handbook of Trace Elements*. St. Lucie Press, Boca Raton, Florida, USA, 223 pp.
- Pansini, M. (1996) Natural zeolites as cation exchangers for environmental protection. *Mineralium Deposita*, **31**, 563–575.
- Prokop, G., Schamann, M. and Edelgaard, I. (2002) *Management of Contaminated Sites in Western Europe*. European Environment Agency, Copenhagen, Denmark, 171 pp.
- Scarpati, C., Cole, P.D. and Perrotta, A. (1993) The Neapolitan Yellow Tuff – A large multiphase eruption from Campi Flegrei, southern Italy. *Bulletin of Volcanology*, **55**, 343–356.
- U.S.D.A. (United States Department of Agriculture - Soil Survey Staff) (1999) *Soil Taxonomy, A Basic System of Soil Classification for Making and Interpreting Soil Surveys*, 2nd edition. Agriculture Handbook No. 436, USDA, Natural Resources Conservation Service, New York, 870 pp.
- Wiers, B.H., Grosse, R.J. and Cilley, W.A. (1982) Divalent and trivalent ion exchange with zeolite A. *Environmental Science & Technology*, **16**, 617–624.

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