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# **Application of neural network model for the prediction of Chromium concentration in phytoremediated contaminated soils**

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## **Abstract**

The assessment of chromium concentrations in plants requires the quantification of a large number of soil factors that affect their potential availability and subsequent toxicity and a mathematical model that predicts their relative concentrations. Many soil characteristics can change the availability of chromium (Cr) to plants in soils. However, accurate, rapid and simple predictive models of metal concentrations are still lacking in soil and plant analysis. In the present work a novel artificial neural network (ANN) model was developed as an alternative rapid and accurate tool for the prediction of Cr concentration in dwarf bean leaves grown in the laboratory on phytoremediated contaminated soils treated with different amendments. First, sixteen (4x4) soil samples were harvested from a phytoremediated contaminated site located in south-western France. Second, a series of measurements were performed on the soil samples. The inputs are the soil amendment, the soil pH, the soil electrical conductivity and the dissolved organic carbon of the soil and the output is the concentration of Cr in the dwarf bean

leaves. Third, an ANN model was developed and its performance was evaluated using a test data set and then applied to predict the exposition of the bean leaves to the Cr concentration versus the soil inputs. The performance of the ANN method was compared with the traditional multi linear regressions method using the training and test data sets. The results of this study show that the ANN model trained on experimental measurements can be successfully applied to the rapid prediction of plant exposition to Cr.

**Key words:** Artificial neural networks (ANN), Soil contamination, Chromium prediction, pH, EC, DOC

## **1. Introduction**

Chromium in plants has received relatively little attention from researchers in comparison with other trace elements such as Cu, Cd, Ni, Al and As. Soils contaminated with Cr have serious consequences for terrestrial ecosystems, agricultural production and human health (Adriano, 2001). Chromium has been considered as the 16<sup>th</sup> most toxic pollutant and it has become a serious health concern because of its carcinogenic and teratogenic effects (Kowalski, 1994). Chromium is also considered a serious environmental pollutant (Kotas and Stasicka, 2000), due to its widespread use in the metallurgical and chemical industries. Improper disposal, poor storage and leakage of Cr from waste discharge through the soil can release Cr to the environment, causing contamination of groundwater and adverse biological and ecological effects.

Chromium is present in the environment in the form of Cr(III) and Cr(VI). These two forms show different chemical, physico-chemical and biochemical properties. Species of Cr(VI) are more soluble, more mobile, more bioavailable and more toxic than Cr(III) (Murti et

al., 1989; Katz and Salem, 1994; Fendorf, 1995; James et al., 1997). This may be due to the fact that Cr(VI) penetrates mammalian cells more readily than Cr(III) (Wetterhahn and Hamilton, 1989). Compounds of Cr(VI) are toxic at low concentrations for both plants and animals. The presence of Cr(VI) in water, soil and wastewater has, therefore, been of great concern. Many factors can influence its migration process, such as pH (McLean and Bledsoe, 1992), dissolved organic carbon or DOC (Heijerick et al., 2003), electrical conductivity or EC (Förstner, 1985) and soil characteristics such as cation exchange capacity, clay content and competition from other metal ions (Sauerbeck and Hein, 1991; Smith, 1994). Soluble chromates are converted to insoluble Cr(III) salts and the subsequent availability for plants decreases (Wetterhahn and Hamilton, 1989). However, soil amendments such as pH (Kabata-Pendias et al., 2000; Jackson et al., 2000), DOC (Hsu et al., 2000), and EC (Laing et al., 2009; Hatje et al., 2003) can be used to change the soil condition and reduce the high concentration of Cr in contaminated soils (Mench and Bes, 2009; Bes and Mench, 2008). Amendments that induce solubility can be used to clean polluted sites by leaching the contaminating trace elements or by facilitating their uptake by plants (phytoextraction) (Kolbas et al., 2011).

Quantifying Cr mobility in a given soil is a critical aspect of predicting its toxicity. Since performing experimental measurements to investigate the relationship between soil parameters and Cr mobility in soil is time-consuming, difficult and expensive, the development of models simulating soil processes has increased rapidly in recent years (Minasny and McBratney, 2002). Generally two common methods are used to develop prediction models, regression methods and artificial neural networks (ANN). Several multiple linear regression (MLR) models have been developed over the past 20 years to predict the sorption of trace metals in soils (van der Zee and van Riemsdijk, 1987; Andersen and Christensen, 1988; Reinds et al., 1995; Streck and Richter, 1997; Römkens and Salomons, 1998; Tiktak et al., 1998; Elzinga et al., 1999; Schug et al., 2000). With MLR methods, the relationships between soil

inputs (properties) and soil output characteristics have to be stated a priori in the regression models. An alternative to MLR is the application of ANN models where such relationships do not need to be formulated beforehand (Anagu et al., 2009; Sarmadian and Taghizadeh Mehrjardi, 2008; Schaap and Leij, 1998; Hambli et al., 2006; Hambli, 2009; Minasny et al., 2004; McBratney et al., 2003; Behrens et al., 2005; Buszewski and Kowalkowski, 2006; Gandhimathi and Meenambal, 2012).

It has been reported that ANNs provide superior predictive performance compared to conventional mathematical methods including MLR models (van der Zee and van Riemsdijk, 1987; Andersen and Christensen, 1988; Streck and Richter, 1997; Römken and Salomons, 1998; Tiktak et al., 1998; Schaap and Lei, 1998; Elzinga et al., 1999; Sarmadian and Taghizadeh Mehrjardi, 2008). In regression models in many soil engineering situations, the input-output relationships are highly complex and are not well understood. The lack of physical understanding and of a powerful general tool for mathematical modeling leads to either simplifying the problem or incorporating several assumptions into mathematical models. Consequently, many mathematical models fail to simulate the complex behavior of most soil engineering problems.

ANNs have been widely used in the field of soil science for prediction of soil hydraulic properties (Schaap et al., 1998; Minasny et al., 2004) generation of digital soil maps (McBratney et al., 2003; Behrens et al., 2005) and modeling of the behavior of trace metals (Buszewski and Kowalkowski, 2006; Anagu et al., 2009; Gandhimathi and Meenambal, 2012). In the cases, ANN are trained to find model input-output relations using an iterative calibration process (training phase). Moreover, ANNs have the advantage of not imposing restrictions on inputs and outputs and can be easily applied to carry out inverse calculation (Jenkins, 1997; Rafiq et al., 2001; Hambli et al., 2006).

In the present study, a novel ANN model was developed as an alternative rapid and accurate tool for the prediction of Cr concentration in dwarf bean leaves (BL) grown in the laboratory on phytostabilized contaminated soils treated with different amendments. The inputs are soil amendment, soil pH, soil EC and soil DOC, whereas the output is Cr concentration in the dwarf BL. The performance of the ANN method was compared with a traditional MLR method using the same training and test data sets. The comparative study revealed that ANN provided a better performance than MLR method in predicting soil properties. Results showed that the neural network model led to a very rapid and accurate prediction of the soil outputs.

## **2. Material and Methods**

### **2.1. Site, soil sampling and soil characterization**

Soil samples were collected from southwestern France, Gironde County (44°43'N; 0°30'W). This site has been contaminated with high concentrations of copper sulfate and chromated copper arsenate. The history of the site and the origin of these pollutants are described in detail by Mench and Bes (2009).

The study site is divided into 15 sub-sites labeled A to E and P1 to P10 depending on total topsoil Cu concentration (Fig. 1a) (Mench and Bes, 2009; Bes et al, 2010). Long-term phytostabilization experiments have been established at the P3 and P7 sub-sites by Bes et al. (2008); Mench and Bes (2009). Plant communities in the zone of the field trial included *Agrostis capillaris*, *Elytrigia repens*, *Rumex acetosella*, *Portulaca oleracea*, *Hypericum perforatum*, *Hypochaeris radicata*, *Euphorbia chamaesyce*, *Echium vulgare*, *Agrostis stolonifera*, *Lotus corniculatus*, *Cerastium glomeratum*, and *Populus nigra* (Bes et al. 2010). The field trial zone (150 m<sup>2</sup>) was established at site P3, which consists of two plots; that were further divided into 16 (3 m x 1 m) sub-plots (Fig. 1b). On these 16 sub-plots, four different

amendments were applied, one per subplot (Latin square design) and carefully mixed in the top soil (0-0.30 m) with a stainless steel spade with four replicates: untreated soil (UNT), 0.2% of dolomite limestone (DL), 5% of compost of poultry manure and pine bark (CPM), and a mixture of 0.2% DL and 5% CPM (DLX CPM). Sixteen soil samples (four replicates) were collected from the four plots treated with the different amendments (4X (UNT), 4X (DL), 4X (OM) and 4X (DLX OM)) to a depth of 0.25 m (Fig. 1b).

Soil pH ( $7.0 \pm 0.23$ ) was measured in a 1:1 soil:water suspension using a glass electrode pH meter (Jackson, 1967). Total nitrogen ( $0.534 \text{ mg kg}^{-1}$ ) was determined at the INRA Laboratoire d'Analyses des sols (LAS), Arras, France using standard methods (INRA LAS, 2007). The organic matter content was determined by a modified Walkely-Blak method: 0.5 g soil was placed in a 500 ml conical flask and mixed with 10 ml of 0.17 M  $\text{K}_2\text{Cr}_2\text{O}_7$ , followed by addition of 20 ml of  $\text{H}_2\text{SO}_4$ , 200 ml of water, 10 ml of  $\text{H}_3\text{PO}_4$  and 1 ml of diphenylamine indicator. Finally, the contents were titrated with 0.5 M  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . The main characteristics of site P3 (0-0.25 m soil layer) are given in Table 1. The cation exchange capacity (CEC) ( $3.49 \text{ Cmol}^+/\text{kg}$ ) was determined using cobaltihexamine chloride (Ciesielski and Sterckeman, 1997). Total metal content in P3 site was determined by ICP-AES after wet digestion with HF and  $\text{HClO}_4$  (AFNOR NF X 31-147; Ciesielski et al., 1997) (Table 1, column 2). Total soil metal concentrations were in the common range of French sandy soil for Cr, As and Zn, but total soil Cu was in excess for these coarse sandy soils (Table 1, column 3). Total Cr concentrations in each of the 16 potted soil samples were measured by laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS). Prior to metal content measurements, the accuracy of the metals determination was checked by performing calibrations with a homogeneous combination of certified reference materials such as NIST-610 (artificial glass), GOR-128-G (komatiite natural glass) and NIST-361 (steel). Little difference was found between the measured and the reference results. In our case, the LA-ICP-

MS measurements produced an averaged error in the range of -1.2% to 1.17%. After the calibration phase, 4 repeated measurements were performed for each soil generating 64 testing results (4 soils  $\times$  4 amendments  $\times$  4 replicates). The precision of the metal content measurement was assessed by the standard deviation (SD) and the coefficient of variation (COV) (Table 2).

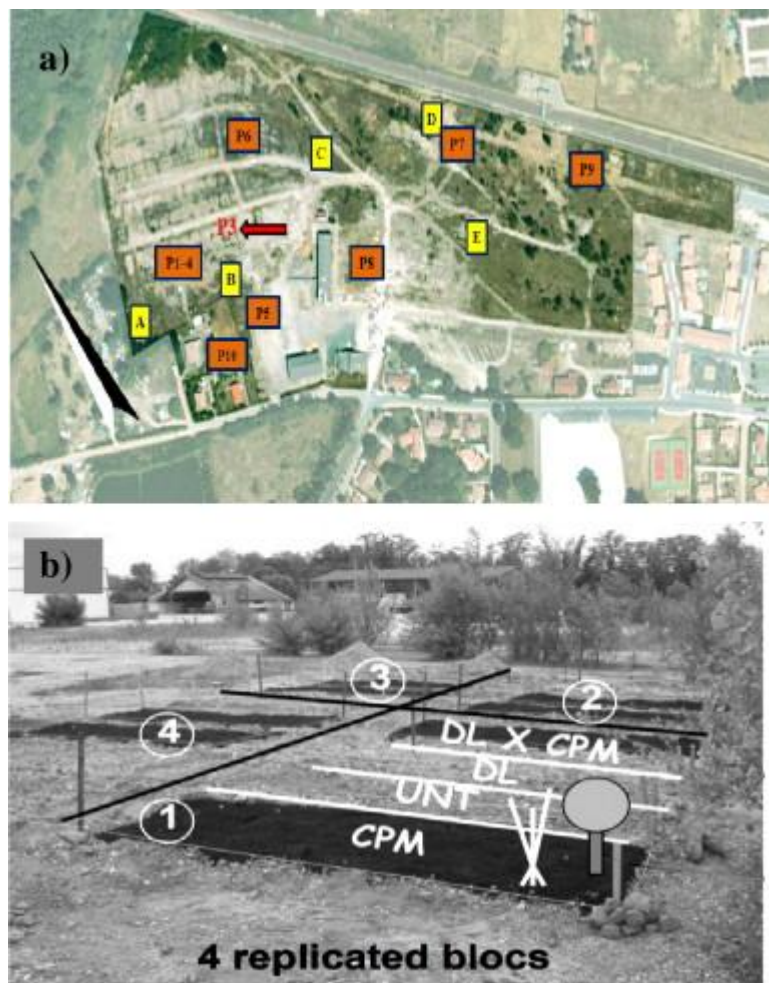


Fig. 1. a) Location of studied sites from A to E. The arrows indicate the studied site P3 (adapted from Mench and Bes, 2009). b) The two plots of soil with the different types of amendment (adapted from Bes, 2008).



Table 1. Main characteristics of site P3 (0–0.25 m soil layer).

Parameters	Site P3	Background values in French sandy soils <sup>a</sup>
Sand %	83.5 ± 1.1	
Silt %	11.5 ± 0.9	
Clay %	3.8 ± 1.2	
C/N	17.2	
OM (g kg <sup>-1</sup> )	15.9	
CEC (cmol <sup>+</sup> kg <sup>-1</sup> )	3.49	
Organic C (g kg <sup>-1</sup> )	9.19	
total N (g kg <sup>-1</sup> )	0.534	
pH	7.0 ± 0.23	
As (mg kg <sup>-1</sup> )	9.8	1.0–25 <sup>b</sup>
Co (mg kg <sup>-1</sup> )	2	1.4–6.8
Cu (mg kg <sup>-1</sup> )	674 ± 126	3.2–4.8
Cr (mg kg <sup>-1</sup> )	23	14.1–40.2
Mn (mg kg <sup>-1</sup> )	181	72–376
Ni (mg kg <sup>-1</sup> )	5	4.2–14.5
Zn (mg kg <sup>-1</sup> )	46	17–48

A : Median and high vibrissae values except for As (Baize, 1997 and Baize and Tercé, 2002).

B : Common As mean values for all French soil types (Baize and Tercé, 2002)

Table 2. The experimental values (pH, EC, DOC and Cr). Four replications were performed for each measurement generating 64 testing results (4 soils × 4 amendments × 4 replicates) allowing for the determination of the mean values, standard deviations (SD) and coefficient of variations (COV).

Soil reference	Amendments	Mean pH	SD-COV (%)	Mean EC ( $\mu\text{S cm}^{-1}$ )	SD-COV (%)	Mean DOC ( $\text{mg l}^{-1}$ )	SD-COV (%)	Mean Cr concentration in the soil ( $\text{mg kg}^{-1}$ )	SD-COV (%)
B1-1	UNT	7.12 NS		1114 NS		15.93 <sup>□</sup>		15.97 <sup>□□</sup>	
B2-8	UNT	7.31 NS		1230 NS		14.34 <sup>□</sup>		16.21 <sup>□□</sup>	
B3-15	UNT	7.28 NS	0.15– 2.08%	917 NS	214.7– 18.31%	21.74 <sup>□</sup>	4.01– 7.75%	15.81 <sup>□□</sup>	0.98– 6.30%
B4-10	UNT	6.99 NS		1430 NS		24.32 <sup>□</sup>		14.07 <sup>□□</sup>	
B1-2	CPM	6.98 NS		1018 NS		27.08 <sup>□</sup>		14.67 <sup>□□</sup>	
B2-5	CPM	7.60 NS		884 NS		20.64 <sup>□</sup>		15.03 <sup>□□</sup>	
B3-16	CPM	7.46 NS	0.27– 3.67%	771 NS	122– 14.24%	25.85 <sup>□</sup>	4.50– 5.44%	15.15 <sup>□□</sup>	0.34– 2.31%
B4-11	CPM	7.26 NS		754 NS		33.99 <sup>□</sup>		14.40 <sup>□□</sup>	
B1-4	DL	7.49 NS		1654 NS		26.34 <sup>□</sup>		17.16 <sup>□□</sup>	
B2-7	DL	7.67 NS	0.14– 1.87%	1000 NS	308.3– 24.79%	25.76 <sup>□</sup>	4.14– 6.96%	16.98 <sup>□□</sup>	0.11– 0.66%
B3-14	DL	7.43 NS		1013 NS		26.52 <sup>□</sup>		17.13 <sup>□□</sup>	

Soil reference	Amendments	Mean pH	SD-COV (%)	Mean EC ( $\mu\text{S cm}^{-1}$ )	SD-COV (%)	Mean DOC ( $\text{mg l}^{-1}$ )	SD-COV (%)	Mean Cr concentration in the soil ( $\text{mg kg}^{-1}$ )	SD-COV (%)
B4-9	DL	7.34 NS		1308 NS		38.46 <sup>□</sup>		16.93 <sup>□□</sup>	
B1-3	DLX CPM	7.45 NS		1192 NS		33.12 <sup>□</sup>		16.09 <sup>□□</sup>	
B2-6	DLX CPM	7.00 NS	0.32– 4.46%	1347 NS	152.2– 11.90%	34.26 <sup>□</sup>	2.50– 7.02%	15.91 <sup>□□</sup>	0.2– 1.27%
B3-13	DLX CPM	7.07 NS		1457 NS		29.16 <sup>□</sup>		15.93 <sup>□□</sup>	
B4-12	DLX CPM	7.59 NS		1119 NS		29.75 <sup>□</sup>		16.35 <sup>□□</sup>	

NS (non significant).

□

Significant for  $p < 0.05$ .

□□

Highly significant for  $p < 0.001$ .

## 2.2. Germination tests

A phyto-toxicological test was applied to the 16 soil samples to assess whether the use of amendments on the field trial zone, assisted by phytostabilisation, is able to reduce the concentrations of bioavailable fractions of Cr for plants. To achieve this objective, one kilo of each soil (4X (UNT), 4X (DL), 4X (OM), 4X (DLX OM)) was placed in a pot after sieving (2

mm). Then, four seeds of dwarf beans (*Phaseolus vulgaris*) were sowed in each potted soil and cultivated for 18 days in controlled conditions (16 h light/8 h darkness). Soil moisture was maintained at around 50% of the field water capacity with additions of deionized water after weighing. Then, the soil moisture was raised to 80% (11-13% of air-dried soil mass) at the beginning of the germination stage of the grains. At the end of the growing period, the plants were harvested and then the dry weights of roots, shoots, and primary leaves were determined after drying at 70 °C.

The dwarf beans were weighed (35-150 mg) directly into Savillex polytetrafluoroethylene PTFE 50 ml vessels. To each vessel 2 ml H<sub>2</sub>O and 2 ml supra-pure 14 M HNO<sub>3</sub> were added and the vessels were heated open at 65 °C for 2 h. Then, the vessel caps were closed and the containers were left overnight at 65 °C (12-14 h). After that they were opened, 0.5 ml of H<sub>2</sub>O<sub>2</sub> (30%) was added to each sample and left at 75 °C open for 3 h. Then, 1.5±0.5 ml of fluorhydric acid HF (48%) was added to each sample, vessel caps were closed and the samples were left at 100 °C overnight. Then, vessels were opened and kept at 120 °C for 4-5 h evaporating to dryness, taken off heat, 1 ml HNO<sub>3</sub> + 5 ml H<sub>2</sub>O + 0.1 ml H<sub>2</sub>O<sub>2</sub> were added to each vessel, gently warmed up and after cooling down made up to 50 ml. Trace element concentrations in digests were determined by ICP-MS (Varian 810-MS) using standard solution of measured trace elements, in our case, Reference Standard Solution of Chromium (1000ppm ±1%/Certified) was used. The accuracy of the metals determination was checked by performing calibrations with standard reference solution. Strong correlation was found between the measured and the reference results ( $R^2=0.998$ ). After the calibration phase, 4 repeated measurements were performed for each digest generating 64 testing results (4 repeated × 16 digests). The precision of the metal content measurement was assessed by the standard deviation (SD) (Table 4), then the Cr concentration in a given dry weight, expressed here, the

mineral masses (g per pot) were determined by multiplying Cr concentration in the BL ( $\text{mg}\cdot\text{kg}^{-1}$ ) in dry weight of BL (g DW) (Table 4).

### **2.3. Characterization of soil solution**

After harvesting the dwarf beans, the soils were watered with distilled water, and maintained daily at 80% of field capacity (11-13% of air-dried soil mass) for 15 days. After 15 days, three Rhizon soil-moisture samplers from Rhizosphere Research Products (Wageningen, Holland) were inserted for 24 h with a  $45^\circ$  angle into each potted soil ( $4 \times 16$  soil) to collect (30 ml) of soil solution from each pot. DOC was analyzed in the solution of soils by a Shimadzu<sup>®</sup> TOC 5000A analyzer. Before DOC measurements, the accuracy of the analyzer was checked by performing calibration with standard reference solution (potassium hydrogen phthalate (KHP) (1000 mg C/L)). In our case, the measurements produced an  $R^2=0.999$ . After the calibration, 4 repeated measurements of DOC were performed for each soil solution. The precision of the DOC measurement was assessed by the SD and the COV (Table 2). Soil pH and EC were determined in the same soil solutions by pH meter and the EC meter (Table 2).

Measured soil variables included soil pH, soil EC, DOC and Cr concentration in the BL with 4 replications for each measurement ( $4 \times 4$  measurements) for the ANN training. Then, a neural network model was developed and trained to predict the exposition of the BL to the high Cr concentration in the soil. The inputs are the soil amendment, soil pH, soil EC and DOC. The output is Cr concentration in the BL.

### **2.4. Selection of soil factors**

The mobility of trace elements plays a major role in the behavior and transfer of metals in soils. Mobility, availability and/or bioavailability of metals is controlled by several factors such as the soil's chemical and physical properties (pH, EC, DOC, temperature, ion charges, etc.), plant species and their related factors (Soon and Bates, 1982; Sauerbeck and Hein, 1991; Davies, 1992, Smith, Fisher, 2002; Weng et al., 2002; Kerndorff, and Schnitzer; 1980; Vogeler et al., 2009). It has been reported that the relationships between the mobility of metal concentrations in plants and a given soil are mainly influenced by the soil properties related to the ion charges (Fisher, 2002; Weng et al., 2002; Kerndorff and Schnitzer; 1980; Vogeler et al., 2009). Therefore, in the current preliminary study, the soil inputs for the ANN model were limited to the three measurable factors considered to be the most influential (pH, DOC and EC) on the mobility and availability of metals in the soil.

Kabata-Pendias et al., (2000) and Jackson et al., (2000) reported that the addition of amendments to soil increased the soil pH compared to the untreated soil, leading to a reduction in the mobility and the availability of metals to plants. The second variable used in our work was DOC. Hsu et al. (2000) noted that the addition of amendment to the soil increased the soil DOC compared to that of untreated soil, which led to increasing plant mass, reducing the bioavailability of metals by forming ligands with dissolved organic matter. The third parameter was EC. Du Laing et al. (2008, 2009) and Hatje et al. (2003) found that an increase in conductivity (salinity) led to increasing the mobility of some metals such as Cd and Zn, thereby increasing the availability and bioavailability of these metals to plants.

To prepare the training data for the ANN, 64 different measurements (4 soils × 4 amendments × 4 replicates) were performed on the four different soils subjected to four different treatments (UNT, DL, CPM and DLX CPM). Because of the noise (uncertainty) concerning the inputs measurement which can be characterized by a given a set of scattered

input data, the 64 experiments were used for the training phase instead of 16 (the total number of experimental replicates) to ensure a more robust processing of the scattered measurements (Table 2).

The 64 experiments were used for the training phase instead of 16 (the total number of experimental replicates) to ensure a more robust processing of the scattered measurements. Presenting the entire patterns (64) ensured the reduction of the ANN prediction sensitivity to noise related to inputs (Velleman, 1980; Kafadar, 1994; Hambli, 2009). The inputs and their minimum/maximum levels are given in Table 3.

Table 3. Selected inputs and output for ANN training (UNT = #1, CPM = #2, DL = #3, DLX CPM = #4).

<b>Inputs</b>	<b>Level</b>	<b>Min value</b>	<b>Max value</b>
Soil treatment	4	#1	#4
pH	4	6.98	7.6
EC ( $\mu\text{S cm}^{-1}$ )	4	754	1654
DOC ( $\text{mg l}^{-1}$ )	4	14.337	34.260
<b>Output</b>			
Cr concentration in the bean leaves ( $\text{mg kg}^{-1}$ )			

## 2.5. Statistical analysis

The total soil solution concentrations of Cr, pH, DOC, EC, foliar elemental concentrations, foliar mineral masses of elements and leaf dry weight (DW) yields were statistically analyzed by ANOVA (Statistica) to evaluate the influence of the treatment and the different effects of soil variables on each other. All analytical determinations were performed in four replicates. Differences were considered statistically significant at  $p < 0.05$ .

## 2.6. Artificial neural network

The ANN architecture is composed of an input layer, a certain number of hidden layers and an output layer in forward connections. Each neuron in the input layer represents a single input parameter. These values are directly transmitted to the subsequent neurons of the hidden layers. The neurons of the last layer represent the ANN outputs (Fig. 2).

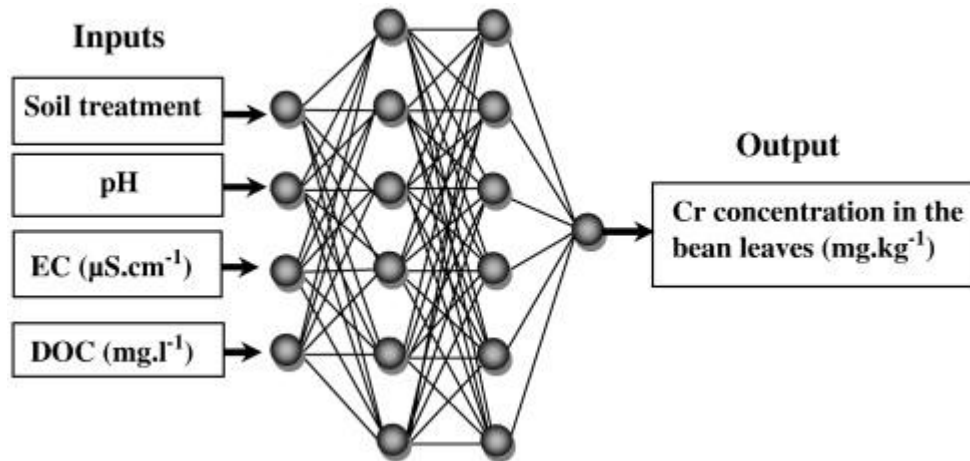


Fig. 2. Neural network architecture composed of four input layers, two hidden layers and one output layer.

The output  $y_i^m$  of neuron  $i$  in a layer  $m$  is calculated by (Jenkins, 1997; Rafiq et al., 2001; Hambli et al., 2006):

$$y_i^m = f(v_i^m) \quad (1)$$

$$v_i^m = \sum_{j=1}^L w_{ji}^{m-1} y_j^{m-1} + b_i^m \quad (2)$$



where  $y_i^0$  are the model inputs,  $v_i^m$  are the outputs of the layer  $m$ ,  $f$  is the activation function,  $L$  is the number of connections to the previous layer,  $w_{ji}^{m-1}$  corresponds to the weights of each connection and  $b_i^m$  is the bias, representing the constant part of the activation function.

Among activation functions, the sigmoid (logistic) function is the one most usually employed in ANN applications. It is given by (Jenkins, 1997; Rafiq et al., 2001; Hambli et al., 2006):

$$f(v_i^m) = \frac{1}{1 + \exp(-\theta v_i^m)} \quad (3)$$

where  $\theta$  is a parameter defining the slope of the function ( $\theta = 0.9$ ).

The training process in ANNs involves presenting a set of examples (input patterns) with known outputs (target output) (Jenkins, 1997; Rafiq et al., 2001; Hambli et al., 2006; Hambli, 2009). The system adjusts the  $w_{ji}^{m-1}$  of the internal connections to minimize errors between the network output and target output (Levenberg-Marquardt back-propagation or BP training algorithm in the current work). The knowledge is represented and stored by the strength (weights) of the connections between the neurons.

In the present work, an in-house ANN program called Neuromod written in Fortran (Hambli et al., 2006; Hambli, 2009) was applied. The basic ANN configuration employed in this study has a double hidden layer with six neurons of each layer with a learning rate factor  $\eta = 0.1$  and momentum coefficient  $\alpha = 0.1$  (Fig. 2). The learning rate coefficient  $\eta$  and the momentum term  $\alpha$  are two user-defined BP algorithm training parameters that affect the learning procedure of the ANN. The training is sensitive to the choice of these net parameters. The learning rate coefficient, employed during the adjustment of  $w_{ji}^{m-1}$ , was used to speed up or slow down the learning process. A larger learning coefficient increases the weight changes, hence large steps

are taken towards the global minimum of error level, while smaller learning coefficients increase the number of steps taken to reach the desired error level. Tests performed for more than two hidden layers and different  $\eta$  and  $\alpha$  parameters showed no significant improvement in the obtained results.

A total of 64 measurements were performed. The proportion of ANN training set from the available data ranged generally from 25% to 80%. The proportion of ANN testing set from the available data is about 15 to 20% and the proportion of the validation data set is about (5 to 15%) (Haykin, 2009). In the current work, the experimental data (64 cases) were subdivided in three sets: 62.5% of the data were used for training (40), 25% for testing (16) and 12.5% for validation (8) covering a wide range of the experiments for validation (2 samples from every experiment variant). The testing data were not used for training. The testing data provided cross validation during the ANN training for verification of the network prediction accuracy. The validation data were used to measure the performance of the predictive capability of the ANN after complete training.

In order to avoid data saturation and artifacts related mainly to the coding of the amendments (non-numeric data), the input and output variables were normalized between 0 and 1 using:

$$x_i^{norm} = \frac{x_i - x_i^{\min}}{x_i^{\max} - x_i^{\min}} \quad (4)$$

where  $x_i$ ,  $x_i^{\min}$ ,  $x_i^{\max}$  and  $x_i^{norm}$  denote, respectively, values of input (output) variables  $i$ , minimum value of input (output) variable, maximum value of input (output) variable and the normalized value of  $i$ .

The de-normalized value of the ANN was computed using:

$$y_t = y_{\min} + y_{norm} (y_{\max} - y_{\min}) \quad (5)$$

where  $y_t$ ,  $y_{\min}$ ,  $y_{\max}$  and  $y_{norm}$  are, respectively, real-valued output variable, minimum and maximum values of real-valued output and the normalized output value from the neural- ANN model.

### 2.6.1. Coding of the amendments

The amendments are model independent inputs, therefore, they can be represented using sequential codes (integer) as a non-numeric indexes from 1 to 4 (UNT=#1, CPM=#2, DL=#3, DLX CPM=#4). Such non-numeric data encoding is common when applying ANN models (Haykin, 2009). An alternative approach is to use the one-of-N encoding technique, which consists of transforming a many-state variable (four states in our case) into several binary variables (one for each state) to represent a single nominal variable. The number of numeric variables equals the number of possible values; one of the  $N$  variables is set to one, and the others are set to zero. In the current case, the input variable “amendment” was replaced by 4 binary variables, (e.g., UNT= 1000, DL= 0100, CPM= 0010, DLX CPM= 0001; where 0 denotes to inactive and 1 active (Ruggiero, 1997)).

In certain cases, a nominal variable with a large number of states would require a prohibitive number of numeric variables for one-of-N encoding, which can increase considerably the ANN size and making the training difficult. If such is the case, it is possible to model the nominal variable using a single numeric sequential encoding if these non-numeric data are inputs. These sequential codes are not quantities or values related to the treatments or any classification of them. In the current ANN model, these codes are treated by the ANN algorithm in the following general form:

- *In case #1 (UNT amendment), the prediction model is determined by the ANN learning phase related to the case 1 representing the UNT treatment.*

- *In case #2 (CPM amendment), the prediction model is determined by the ANN learning phase related to the case 2 representing the CPM treatment.*
- *In case #3 (DL amendment), the prediction model is determined by the ANN learning phase related to the case 3 representing the DL treatment.*
- *In case #4 (DLX CPM amendment), the prediction model is determined by the ANN learning phase related to the case 4 representing the DLX CPM treatment.*

In addition, during the training phase the assigned codes for the amendments [1, 4] are converted in the normalized range [0, 1] using Eq. (4) to avoid coding artificial effects and de-normalized after prediction in the range of [1, 4] using Eq. (5).

## **2.7. Multiple linear regression model**

The most common method used to quantify relationships between inputs and outputs is to employ multiple linear regressions in the form:

$$Y_i = \alpha_i + \sum_{j=1}^n \beta_j X_{ij} \quad (6)$$

where  $Y_i$  is the output variable  $i$ ,  $X_{ij}$  are the input variables related to the sample,  $i$ ,  $\alpha_i$  and  $\beta_j$  are the model regression coefficients determined by a fitting procedure using generally least squares method.

## **3. Results and Discussion**

### **3.1 Experimental results**

### 3.1.1 Soil solution characteristics

Table 2 shows the physico-chemical parameters (i.e., pH, DOC and EC) of the 16 soil solutions and the total soil Cr concentration measured in the 16 contaminated soils. These measurements concerned the 16 pots containing the 16 types of soils: 4X UNT, 4X DL, 4X CPM, and 4X DLX CPM. Amendment incorporation into the soil increased soil pH slightly in the treated soil compared to the untreated one. This effect was in decreasing order based on mean values from 4 replicates): DL ( $7.5 \pm 0.14$ ) > CPM ( $7.4 \pm 0.27$ ) > DLX CPM ( $7.3 \pm 0.29$ ) > UNT ( $7.2 \pm 0.15$ ). The organic matter added to the soil (i.e., CPM) resulted in reduction of EC ( $856.75 \pm 122.00 \mu\text{S}\cdot\text{cm}^{-1}$ ) compared to the DL ( $1243.75 \pm 308.27 \mu\text{S}\cdot\text{cm}^{-1}$ ), DLX CPM ( $1278.75 \pm 152.18 \mu\text{S}\cdot\text{cm}^{-1}$ ) and the UNT ( $1172.75 \pm 214.72 \mu\text{S}\cdot\text{cm}^{-1}$ ). The soil amendments had no significant effect on the pH and EC of the four types of soil. In contrast, the addition of amendments significantly increased the DOC in the soil solution compared to the untreated soil ( $p = 0.019$ ). This effect was in the following order: DLX CPM ( $34.6 \pm 2.50 \text{ mg}\cdot\text{l}^{-1}$ ) > DL ( $29.2 \pm 6.14 \text{ mg}\cdot\text{l}^{-1}$ ) > CPM ( $26.8 \pm 5.49 \text{ mg}\cdot\text{l}^{-1}$ ) > UNT ( $19.0 \pm 4.72 \text{ mg}\cdot\text{l}^{-1}$ ). The amendments also had a significant effect on the total Cr concentration in the soils ( $p = 0.000501$ ). A good correlation was observed between soil pH and DOC ( $R^2 = 0.589$ ), but poorer or lack of correlations were observed between the other variables used in our experiment.

### 3.1.2. Concentration and Mineral mass of Cr in the bean leaves

Table 4 shows that the measured Cr concentrations in the BL were less than the toxic concentrations measured in the tops of plants reported by Kitagishi and Yamane (1981), Gough et al. (1979) and Davis et al. (1978). The mean value of foliar Cr concentrations in the beans decreased from  $1.438 \pm 1.23$  in the UNT soil to  $0.733 \pm 0.08$  in the soil amended with CPM, to

0.588±0.17 in the soil amended with DL and to 0.652±0.012 in the soil amended with DLX CPM. However, the soil amendments (CPM, DL, DLX CPM) had no significant effects on the Cr concentrations in the BL ( $p= 0.436$ ) (Table 4).

Leaf Cr mineral mass ( $\text{g}\cdot\text{ha}^{-1}$ ) was computed with foliar Cr concentrations ( $\text{mg}\cdot\text{kg}^{-1}$  DW) and foliar biomass ( $\text{g}$  DW per pot). We can clearly note in Table that soil amendments decreased the mineral mass of Cr in the BL compared to the UNT plants ( $0.094\pm 0.03$  g per pot). The lowest Cr mineral masses were observed for the DLX CPM plants ( $0.067\pm 0.01$  g per pot). This difference in the mineral masses is notably driven by the lower foliar Cr concentrations and dry weight in the DLX CPM plants. The DL and DLX CPM additions decreased the Cr mineral masses more than those for CPM and UNT. While amendments added to soil had a significant effect on the total Cr concentration ( $p=0.000501$ ) in the four soils UNT ( $15.52$   $\text{mg}\cdot\text{kg}^{-1}$ ), CPM( $14.81$   $\text{mg}\cdot\text{kg}^{-1}$ ), DL( $17.05$   $\text{mg}\cdot\text{kg}^{-1}$ ) and DLX CPM( $16.07$   $\text{mg}\cdot\text{kg}^{-1}$ ), there was no significant effect of soil amendments on the concentration and the mineral masses of Cr in the plants.

Table 4. Dry weight (g), concentration ( $\text{mg kg}^{-1}$ ) and mineral mass of Cr (g per pot) measured in the BL.

Soil amendments	Dry weight (g)	Cr concentration in the plant ( $\text{mg kg}^{-1}$ )	Mineral mass (g per pot)
UNT	$0.087 \pm 0.04$	$1.438 \pm 1.23$	$0.094 \pm 0.03$
CPM	$0.112 \pm 0.02$	$0.733 \pm 0.08$	$0.083 \pm 0.01$
DL	$0.122 \pm 0.02$	$0.588 \pm 0.17$	$0.069 \pm 0.00$
DLX CPM	$0.103 \pm 0.00$	$0.652 \pm 0.012$	$0.067 \pm 0.01$

### 3.2. Neural network modeling results

The ANN was trained with  $3 \times 10^4$  epochs (number of training cycles). The training performance was assessed by the root mean square error (RMSE). At the end of the training phase, the RMSE convergence value was  $1 \times 10^{-5}$ . Table 5 shows the experimental and ANN predicted values of Cr concentration in the BL for the four soil groups (four different amendments) and their corresponding correlation coefficients.

Table 5. Comparison between averaged measured and ANN predicted values of Cr concentration in the bean leaves for the four soil groups. The determination coefficient  $R^2$  is based on the eight experimental samples kept for validation.

<b>Soil (UNT)</b>		<b>Soil (CPM)</b>		<b>Soil (DL)</b>		<b>Soil (DLX CPM)</b>	
<b>Measured</b>	<b>NN</b>	<b>Measured</b>	<b>NN</b>	<b>Measured</b>	<b>NN</b>	<b>Measured</b>	<b>NN</b>
3.29	3.285	0.762	0.764	0.519	0.519	0.524	0.523
0.748	0.746	0.709	0.710	0.775	0.773	0.819	0.820
0.601	0.600	0.392	0.391	0.892	0.890	0.805	0.804
0.661	0.662	0.498	0.496	0.618	0.616	0.781	0.780
$R^2 = 0.9998$		$R^2 = 0.9986$		$R^2 = 0.9989$		$R^2 = 0.9991$	

An average correlation coefficient of 0.9998 between the measured and ANN predicted values as found. This indicates that the ANN model was able to predict the Cr concentration in the BL rapidly and accurately. In order to investigate the effects of the soil amendments, soil pH, soil EC and DOC inputs on the Cr concentration in the BL, a parametric study of the ANN output with respect to the inputs was performed for each soil treatment with the trained ANN. For each input factor, four values in the interval between the minimum and maximum values of each input were applied here to capture the non-linear response (Table 6). Full factorial design generated 256 ( $4 \times 4 \times 4 \times 4$ ) combinations to study the effect of each input on the Cr response. The computation time was about 2 seconds.

Table 6. Selected four inputs for the ANN prediction. Full factorial combinations generate 256 ( $4 \times 4 \times 4 \times 4$ ) data to investigate their effects on soil response.

<b>Inputs</b>	<b>Min</b>	<b>Max</b>	<b>Level 1</b>	<b>Level 2</b>	<b>Level 3</b>	<b>Level 4</b>
Soil treatment #1	#4	UNT	CPM	DL	DLX	CPM
pH	6.98	7.6	7.0	7.2	7.4	7.6
EC ( $\mu\text{S cm}^{-1}$ )	754	1654	800	1100	1400	1600
DOC ( $\text{mg l}^{-1}$ )	14.337	34.260	14	20	28	34

To explore the relationships between the inputs and the output, several response surfaces (RS) were plotted consisting of 3D graphical representation of a response between two independent variables (inputs) and the output. The 3D RS plots provide insight into the behavior of the system and enable investigation of the parametric Cr concentration results versus the levels of the effecting factors predicted by the ANN model. Figure 3 shows the coupled effects of the pH and EC on the Cr concentration in BL for two different values of DOC (14 and 34  $\text{mg.l}^{-1}$ ).



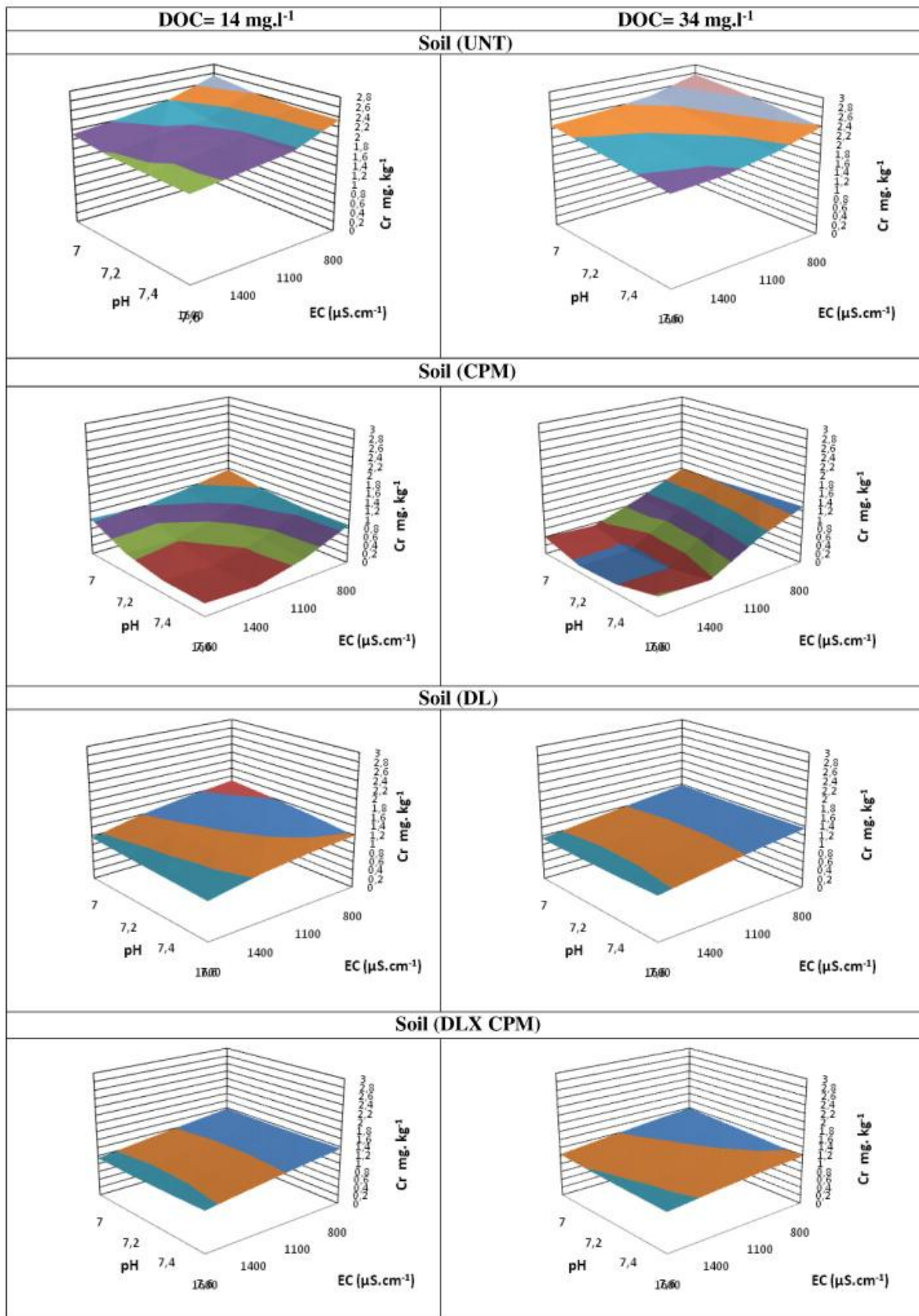


Fig. 3. Chromium concentration in BL in mg kg<sup>-1</sup>: effects of soil pH and EC for two different limit values of DOC.

The predicated Cr concentration depends strongly on the soil factors and the type of amendments. It can be seen in the left-hand column of Figure 3 that soil amendments (CPM, DL and DLX CPM) and other factors such as pH, EC and low DOC (DOC=14 mg.l<sup>-1</sup>) decreased the Cr concentration in the BL to 1, 1.2 and 1.4 mg.kg<sup>-1</sup>, respectively, compared to the untreated soil which presents a reference Cr concentration of about 2.4 mg.kg<sup>-1</sup>. The same effect of soil amendments can be observed when the DOC value increased to 34 mg.l<sup>-1</sup> (Fig. 3 right-hand column). If we compare the right and left columns of Figure 3, we can see that the increase in DOC concentration from 14 to 34 mg.l<sup>-1</sup> in the soil slightly increased the availability of Cr to plants in the treated (CPM, DL, DLX CPM) and UNT soils by 0.3, 0.2, 0.2, 0.4 mg.kg<sup>-1</sup>, respectively.

Barcelona and Holm (1991), Pansar-Kallio et al. (2001) and Seaman et al. (2001) reported that oxidation and reduction reactions are important in the fate, transport, and toxicity of Cr in the soil. These reactions are governed by many factors including organic matter, pH, aeration, soil moisture content, wetting and drying, microbial activity, the content in clay minerals and availability of electron donors and acceptors. Moreover, the amendments added to the soil have the capacity to change the Cr from Cr(VI), which has a high mobility and toxicity and facilitates leaching, to Cr(III), which is relatively insoluble and resistant to leaching (James et al., 1997). Fendorf (1995) also reported that the reduction of Cr in soils is accelerated by the presence of organic matter and divalent iron. If Cr in the soil is converted to trivalent oxide or co-precipitated with Fe hydrous oxide or organic matter, it is likely to remain stable for a long time. Our results agree with those of Hsu et al. (2000), who reported that the high affinity of metals for CPM had two-sided consequences. The first is that in the presence of DOC the mobility of trace elements increases by forming complexes with the humic acid and fulvic acid, leading to the high mobility and availability of metals to plants. Secondly, non soluble high

molecular weight organic acids can retain significant concentrations of trace metals in soil upon soil acidification, thus decreasing their mobility (Chirenje et al., 1999).

The concurrent effect of the three studied factors can be observed clearly in the soil treated with CPM (Fig. 3- right-hand column), where it can be seen that the increase in the DOC value ( $34 \text{ mg.l}^{-1}$ ) led to an increase in the Cr availability to the plant from  $1.2\text{-}1.4 \text{ mg.kg}^{-1}$  in the case of  $\text{DOC}=34 \text{ mg.l}^{-1}$  compared to soil treated with CPM containing less DOC ( $14 \text{ mg.l}^{-1}$ ) where it decreased from  $1.2$  to  $0.8 \text{ mg.kg}^{-1}$ . The increase in pH leads to a slight decrease in Cr concentration in plants, whereas the decrease in EC leads to a strong increase in Cr concentration in the BL from  $0.2$  at  $\text{EC}=1100 \text{ mg.kg}^{-1}$  to  $1.3$  at  $\text{EC}=800 \text{ mg.kg}^{-1}$  in the case of  $\text{DOC}=34 \text{ mg.l}^{-1}$ . This result can be explained by the fact that in the case of anions ( $\text{Cr(VI)}$ ), the decrease in pH promotes the release of  $\text{HO}^-$  ions. This then leads to a decrease in competition between anions and  $\text{HO}^-$  ions, which then accelerates the formation of new phases. Thus, the solubility of Cr anions decreases when pH decreases. Dzombak and Morel (1990) reported that when soil pH increases, the mobility of metals decreases, thereby decreasing the uptake of Cr by living species as in the case of soil treated with DL, CPM at  $\text{DOC}=14 \text{ mg.l}^{-1}$ . Another important factor that has a major effect on the bioavailability of Cr is EC. Increases in chloride, sulfate, carbonate, bicarbonate, nitrate and phosphate concentrations in solution lead to the formation of metallic salts, which increase the EC of the soil solution. An increase in salinity is associated with an increase in the concentration of major elements (Na, K, Ca, Mg), which compete with trace metals for sorption sites (Tam and Wong, 1999). This is different from our results where we found that the increase in DOC and pH and decrease in EC lead to an increase in Cr concentration in plants.

The predicted findings suggest that due to the large variation of Cr concentration in the BL with different treatments, the best amendment for reducing soil Cr toxicity is the (CPM) treatment. This reduced Cr concentration from  $2.4 \text{ mg.kg}^{-1}$  in the untreated soil to  $1 \text{ mg.kg}^{-1}$

(case of  $\text{DOC}=14 \text{ mg.l}^{-1}$ ) and from  $2.8 \text{ mg.kg}^{-1}$  in the untreated soil to  $1.2 \text{ mg.kg}^{-1}$  (case of  $\text{DOC}=34 \text{ mg.l}^{-1}$ ). These two DOC values result in non-linear Cr variation versus pH and EC. However, the DL and DLX CPM treatments generated intermediate Cr concentration levels but with a more stable (linear) variation compared to that of the CPM treatment.

When all the results are considered, it can be seen that the Cr tends to evolve from non-linear responses for UNT and CPM soils to linear responses for DL and DLX CPM soils. UNT soil generated the highest non-linear variation in Cr concentration, suggesting that the results are sensitive to pH and EC. Such a variation is reduced, however, with the addition of CPM and DL or with a combined treatment (DLX CPM). We found that among the investigated factors, pH and DOC are the most important parameters affecting the Cr concentration in BL.

However, there are only a limited number of published studies available for describing the techniques of stabilization of Cr in the soil. Because of the low reactivity of its common species in soils, even if Cr is added to soil in the mobile form Cr(VI), it can be converted to its stable form Cr(III). Jop et al. (1987) reported that the dominant species of Cr(VI) at  $\text{pH} > 6.5$  is chromium oxide (the case of our soil). As Cr(VI) species are negatively charged, they do not complex with anionic particulate matter and are more bioavailable. In our experience, we have noted that the addition of both organic and inorganic amendments to the soil can decrease the bioavailability of Cr with reference to untreated soil.

### **3.3. Comparison of MLR and ANN performance**

Four MLR experiments were performed, one each of the four soil training data pertaining to every amendment, to quantify the relationships between Cr concentration in BL

and the soil factors (pH, EC and DOC). The software used for the purpose of statistical analyses was Statistica 10. These four MLR equations are:

<b>Amendment</b>	<b>MLR equations per amendment</b>
<b>UNT</b>	$Y_{BL} = 2.255 + 0.0623 \times x_{pH} - 6.44e^{-4} \times x_{EC} + 0.00128 \times x_{DOC}$
<b>DL</b>	$Y_{BL} = 2.987 - 0.113 \times x_{pH} - 1.26e^{-3} \times x_{EC} + 0.00097 \times x_{DOC}$
<b>CPM</b>	$Y_{BL} = 1.851 + 0.0124 \times x_{pH} - 6.67e^{-4} \times x_{EC} + 0.00115 \times x_{DOC}$
<b>DLX CPM</b>	$Y_{BL} = 1.986 + 0.0118 \times x_{pH} - 6.61e^{-4} \times x_{EC} + 0.00101 \times x_{DOC}$

where  $x_{pH}$ ,  $x_{EC}$  and  $x_{DOC}$  denote, respectively, values of pH, EC and DOC.

After determining of these equations, comparison between predictive results of the ANN and MLR models was performed for the training and test data sets. The obtained coefficients of correlations among the results (Table 7). This indicates that the results of ANN model are better than that of MLR models for all amendment cases. Our finding agrees well with those of van der Zee and van Riemsdijk (1987), Andersen and Christensen (1988), Streck and Richter (1997), Römken and Salomons (1998), Tiktak et al. (1998), Schaap and Lei (1998), Elzinga et al. (1999), Sarmadian and Taghizadeh Mehrjardi (2008).

Table 7. Correlation coefficients obtained by ANN and MLR methods.

<b>Method</b>	<b>UNT</b>		<b>CPM</b>		<b>DL</b>		<b>DLX CPM</b>	
	<b>Trainin g data</b>	<b>Trainin g data</b>	<b>Trainin g data</b>	<b>Trainin g data</b>	<b>Trainin g data</b>	<b>Trainin g data</b>	<b>Trainin g data</b>	<b>Trainin g data</b>
Neural network	0.999	0.998	0.998	0.996	0.998	0.997	0.999	0.995
Linear regressio n	0.876	0.695	0.792	0.702	0.765	0.637	0.882	0.802

#### 4. Conclusion

Reducing the concentration of Cr in contaminated soils can be performed by adding soil amendments. These amendments reduce Cr mobility by promoting the formation of insoluble precipitates or by enhancing the soil's capacity to bind Cr to the soil. The latter can be achieved directly through the addition of adsorbent materials or indirectly by adjusting the soil's pH–EC combination to provoke Cr absorption onto the soil. In this preliminary study, three factors were retained (pH, EC and DOC) in combination with four soil amendments (UNT, CPM, DL and DLX CPM). The present study confirmed that organic matter (CPM) is one of the best soil amendments, as it reduced the concentrations of Cr in the BL more than the other amendments. The interactions of the soil factors in the form of response surfaces were analyzed and compared to existing published results. This methodology could be effectively used to study the importance of individual, cumulative and interactive effects of the selected soil inputs in Cr concentration in bean leaves. The predictive ANN models used to evaluate the Cr concentration corresponded well with the experimental results reported in the literature. The ANN models developed here showed that a plausible innovative low-cost strategy for in situ remediation of Cr contaminated soils using organic and inorganic amendments, modified vegetation, or a combination of the two approaches. It should be noted that the ANN approach proposed here does not take into account all the possible factors that may influence soil toxicity. The primary aim was to illustrate the potential of the ANN method in its ability for rapid and accurate prediction of soil toxicity. The ANN model can be extended by including additional factors and their combinations to capture complex Cr behavior.

Overall, the ANN modeling outperforms MLR modeling. The effort required to calibrate the ANN and MLR models were similar, and both require about the same amount of time and processing resources. Despite their good performance, ANNs suffer from a number of

limitations. First, they are not able to explain the physical relationships between the input-output data. Secondly, there are no general guidelines for the design of ANN architecture for a given problem. There is a need for more research to develop such guidelines to enable the extensive application of ANNs for non-specialists. Nevertheless, ANNs have a number of significant benefits that make them a powerful, rapid and practical tool for solving many soil engineering problems. The implementation of ANN modeling for the robust and reliable prediction of metal concentration in plants using additional soil data such as soil particle size and moisture levels in a practical sensor system appears very promising. Future significant work is required to achieve this goal. The results of ANN testing (prediction) allow for the investigation of the soil factors' interactions. This methodology could therefore be effectively used to study the importance of individual, cumulative and interactive effects of the soil parameters. Moreover, the ANN method can be used in conjunction with mechanistic models at the research level as a method to determine the most important parameters in a design that could then be used to formulate a mechanistic model and to determine where future research efforts should be directed.

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## References

- Adriano, D.C., 2001. Trace elements in terrestrial environments; Biochemistry, bioavailability and risks of metals. Springer-Verlag, New York.
- AFNOR NF X 31-147 : (Qualité des sols) : Sols, sédiments – Mise en solution totale par attaque acide.
- Anagu, I., Ingwersen, J., Utermann, J., Streck, T., 2009. Estimation of heavy metal sorption in German soils using artificial neural networks. *Geoderma* 152, 104–112.
- Andersen, P.R., Christensen, T.H., 1988. Distribution coefficients of Cd, Co, Ni and Zn in soils. *Journal of soil science* 39, 15-22.
- Baize, D., 1997. Un Point sur Les Teneurs Totales des Eléments Traces Métalliques dans les Sols, INRA Editions, Paris, France, pp 408.
- Baize, D., Tercé, M., 2002. Les Éléments Traces Métalliques dans les Sols – Approches Fonctionnelles et Spatiales, INRA Éditions, Paris, France. pp 570.
- Barcelona, M.J., Holm, T.R., 1991. Oxidation–reduction capacities of aquifer solids. *Environmental science and technology* 25, 1565–1571.
- Behrens, T., Förster, H., Scholten, T., Steinrücken, U., Spies, E., Goldschmitt, M., 2005. Digital soil mapping using artificial neural networks. *Journal of plant nutrition and soil science* 168, 21-33.
- Bes, C., Mench, M., 2008. Remediation of copper-contaminated topsoils from a wood treatment facility using in situ stabilisation. *Environmental Pollution* 156, 1128-1138.
- Bes, C., 2008. Phytoremédiation des sols d'un site de traitement du bois contaminé par le cuivre. Ph.D. Dissertation, Université de Bordeaux1, Talence, France.



- Bes, C.M., Mench, M., Aulen, M., Gaste, H., Taberly, J., 2010. Spatial variation of plant communities and shoot Cu concentrations of plant species at a timber treatment site. *Plant Soil* 330, 267–80.
- Buszewski, B., Kowalkowski, T., 2006. A new model of heavy metal transport in the soil using non-linear artificial neural networks. *Journal of environmental engineering science* 23 (4), 589-595.
- Chirenje, T., Ma, L.Q., 1999. Effects of acidification on metal mobility in a papermill-ash amended soil. *Journal of Environmental Quality* 28, 760–767.
- Ciesielski, H., Sterckeman, T., 1997. Determination of exchange capacity and exchangeable cations in soils by means of cobalt hexamine trichloride. Effects of experimental conditions, *Agronomie* 17, 1-7.
- Ciesielski, H., Proix, N., Sterckeman, T., 1997. Détermination des incertitudes liées à une méthode de mise en solution des sols et des sédiments par étude inter laboratoire. *Analisis* 25, 6, 188-192.
- Davis, R.D., Beckett, P.H.T., Wollan, E., 1978. Critical levels of twenty potentially toxic elements in young spring barley. *Plant Soil* 49, 395-408.
- Davies, B.E., 1992. Inter-relationships between soil properties and the uptake of cadmium, copper, lead and zinc from contaminated soils by radish (*Raphanus sativus* L.). *Water, Air, Soil Pollution* 63,331-342.
- Du Laing, G., De Vos, Vandecasteele, B., Lesage, E., Tack, F.M.G., Verloo, M.G., 2008. Effect of salinity on heavy metal mobility and availability in intertidal sediments of the Scheldt estuary. *Estuarine coastal and shelf science* 77, 589–602.
- Du Laing, G., Van de Moortel, A., Moors, W., De Grauwe, P., Meers, E., Tack, F., Verloo, M., 2009. Factors affecting metal concentrations in reed plants (*Phragmites australis*) of intertidal marshes in the Scheldt estuary. *Ecological engineering* 35, 310-318.

- Dzombak, D.A., Morel, F.M.M., 1990. Surface Complexation Modeling - Hydrous Ferric Oxide. John Wiley & Sons (A Wiley-Interscience Publication), pp 393.
- Elzinga, E.J., Van Grinsven, J.J.M., Swartjes, F.A., 1999. General purpose Freundlich isotherms for cadmium, copper and zinc in soils. *European Journal of Soil Science* 50, 139-149.
- Fendorf, S., 1995. Surface reactions of chromium in soils and waters. *Geoderma* 67, 55-71.
- Fischer, K. Removal of heavy metals from soil components and soil by natural chelating agents. 2000, Part 1: Displacement from clay minerals and peat by L-cysteine and L-penicillamine. *Water, Air, Soil Pollution* 137, 267.
- Förstner, U., 1985. Chemicals forms and reactivities of metals in sediments in "chemical methods for assessing bio-available metals in sludges and soil", Leschber R., Davis R.D., L'Hermite P., CEC, Elsevier Applied Science publishers, 1-30.
- Gandhimathi, A., Meenambal, T., 2012. Analysis of Heavy Metal for Soil in Coimbatore by using ANN Model. *European Journal of Scientific Research* 68, (4), 462-474.
- Gough, L.P., Shacklette, H.T., Case, A.A., 1979, Element Concentrations Toxic to Plants, Animals, and Man, US Geological Survey Bulletin 1466, 80.
- Hambli, R., 2009. Statistical damage analysis of extrusion processes using finite element method and neural networks simulation. *Finite Elements in Analysis and Design* -45- 10, 640-649.
- Hambli, R., Chamekh, A., Bel Hadj Salah, H., 2006. Real-time deformation of structure using finite element and neural networks in virtual reality applications, *Finite Elements in Analysis and Design* 42, (11), 985-991.
- Hatje, V., Payne, T.E., Hill, D.M., McOrist, G., Birch, G.F., Szymczak, R., 2003. Kinetics of trace element uptake and release by particles in estuarine waters: effects of pH, salinity, and particle loading. *Environment International* 29, 619–629.

- Haykin, S., 2009. Neural Networks and learning machine (3rd Edition), Pearson, 936 p.
- Heijerick, D.G., Janssen, C.R., De Coen, W.M., 2003. The combined effects of hardness, pH and dissolved organic carbon on the chronic toxicity of Zn to *D. magna*: development of a surface response model. *Archives of Environmental Contamination and Toxicology* 44, 210–217.
- Hsu, J.H., Lo, S.L., 2000. Characterisation and extractability of copper, manganese, and zinc in swine manure composts. *Journal of Environmental Quality* 29 (2), 43–48.
- Jackson, M.L., 1967. *Soil Chemical Analysis*. Prentice Hall of India Pvt. Ltd., New Delhi, pp 49.
- Jackson, B.P., Miller, W.P., 2000. Soil solution chemistry of a fly ash-, poultry litter-, and sewage sludge-amended soil. *Journal of Environmental Quality* 29 (2), 430–436.
- James, B.R., Petura, J.C., Vitale, R.J., Mussoline, G.R., 1997. Oxidation-reduction chemistry of chromium: Relevance to the regulation and remediation of chromate contaminant soils. *Journal of soil contamination* 6, 569-580.
- Jenkins, W.M., 1997. An introduction to neural computing for the structural engineer. *Journal of structural engineering* 75 3, 38-41.
- Jop, K.M., Parkerton, T.F., Rodgers, J.H.Jr., Dickson, K.L., 1987. Comparative toxicity and speciation of two hexavalent chromium salts in acute toxicity tests. *Journal of environmental toxicology and chemistry* 6, 697-703.
- Kabata-Pendias, H., Pendias, 2000. *Trace Elements in Soils and Plants*. CRC Press, Boca Raton, Florida, USA.
- Kafadar, K., 1994. Choosing among two-dimensional smoothers in practice. *Computational Statistics and Data Analysis* 18, 419-439.

- Katz, S.A., Salem, H., 1994. The biological and environmental chemistry of chromium. VCH Publishers, Inc., New York.
- Kerndorff, H., Schnitzer, M., 1980. Sorption of metals on humic acids. *Geochimica et Cosmochimica Acta* 44,1701.
- Kitagishi, K., Yamane, I (Eds.), 1981. Heavy Metal Pollution in Soils of Japan, Japan Scientific Societies Press, Tokyo, 107–124.
- Kolbas, A., Mench, M., Herzig, R., Nehnevajova, E., Bes, C.M., 2011. Copper phytoextraction in tandem with oilseed production using commercial cultivars and mutant lines of sunflower. *International Journal of Phytoremediation* 13 Suppl 1, 55-76.
- Kotas, J., Stasicka, Z., 2000. Commentary: chromium occurrence in the environment and methods of its speciation. *Environmental Pollution*, 107, 263– 83.
- Kowalski, Z. J., 1994. Treatment of chromic tannery wastes. *J Hazard Mater* 37: 137-144.
- McBratney, A.B., Mendoca Santos, M.L., Minasny, B., 2003. On digital soil mapping. *Geoderma* 117, 3-52.
- McLean, J.E., Bledsoe, B.E., 1992. Behaviour of metals in soils. Ground water issue, USEPA, Washington, DC. EPA/540/S-92/018.
- Mench, M., Bes, C., 2009. Assessment of ecotoxicity of topsoils from a wood treatment site. *Pedosphere* 19,143–155.
- Minasny, B., McBratney, A.B., 2002. The neuro-m methods for fitting neural network parametric pedotransfer functions. *Soil Science Society of America Journal* 66, 352-361.
- Minasny, B., Hopmans, J.W., Harter, T., Eching, S.O., Tuli, A., Denton, M.A., 2004. Neural networks prediction of soil hydraulic functions for alluvial soils using multistep outflow data. *Soil Science Society of America Journal* 68, 417—429.
- Murti, K., Viswanathan, C.R., Puspa., 1989. Toxic Metals in the Indian environment and its human health implication. Tata Mc Graw Hill Publication, 131-148.

- Pantsar-Kallio, M., Reinikainen, S.P., Oksanen, M., 2001. Interactions of soil components and their effects on speciation of chromium in soils. *Analytica Chimica Acta* 439, 9–17.
- Rafiq, M.Y., Bugmann G., Easterbrook, D. J., 2001. Neural network design for engineering applications. *Computers & Structures*, 79, (17), 1541-1552.
- Reinds, G.J., Bril, J., De Vries, W., Groenenberg, J.E., Breeuwsma, A., 1995. Critical loads and excess loads of cadmium, copper and lead for European forest soils. DLO Winand Staring Centre Report 96, Wageningen, the Netherlands.
- Ruggiero, M.A., 1997. *Cybernetic Trading Strategies*, John Wiley & Sons, 336 pages ISBN 0471149209.
- Römken, P.F.A.M., Salomons, W., 1998. Cd, Cu and Zn solubility in arable and forest soils: consequences of land use changes for metal mobility and risk assessment. *Soil Science* 163, 859-871.
- Sarmadian, F., Taghizadeh Mehrjardi, R., 2008. Modeling of Some Soil Properties Using Artificial Neural Network and Multivariate Regression in Gorgan Province, North of Iran, *Global Journal of Environmental Research* 2 (1), 30-35.
- Sauerbeck, D. R., Hein, A., 1991. The nickel uptake from different soils and its prediction by chemical extractions. *Water Air Soil Pollution* 57-58, 861-871.
- Schaap, M.G., Leij, F.J., 1998. Using neural networks to predict soil water retention and soil hydraulic conductivity. *Soil and Tillage Research* 47, 37-42.
- Schaap, M.G., Leij, F.J., van Genuchten, M.T., 1998. Neural networks analysis for hierarchical prediction of soil hydraulic properties. *Soil Science Society of America Journal* 62, 847—855.
- Schug, B., Düring, R.A., Gäth, S., 2000. Improved cadmium sorption isotherms by the determination of initial contents using the radioisotope <sup>109</sup>Cd. *Journal of plant nutrition and soil science* 163, 197–202.

- Seaman, J.C., Arey, J.S., Bertsch, P.M., 2001. Immobilization of nickel and other metals in contaminated sediments by hydroxyapatite addition. *Journal of Environmental Quality* 30 (2), 460–469.
- Smith, S. R., 1994. Effect of soil pH on availability to crops of metals in sewage sludge-treated soils. 1. Nickel, copper and zinc uptake and toxicity to ryegrass. *Journal of environmental pollution* 85, 321-327.
- Soon, Y. K., Bates, T. E., 1982. Chemical pools of Cd, Ni and Zn in polluted soils and some preliminary indications of their availability to plants. *Soil Science* 33, 477-88.
- Streck, T., Richter, J., 1997. Heavy metal displacement in a sandy soil at the field scale: I. Measurements and parameterization of sorption. *J. Environ. Qual* 26, 49—56.
- Tam, NFY., Wong, YS., 1999. Mangrove soils in removing pollutants from municipal wastewater of different salinities. *Journal of environmental quality* 28, 556-564.
- Tiktak, A., Alkemade, J.R.M., Van Grinsven, J.J.M., Makaske, G.B., 1998. Modeling cadmium accumulation at a regional scale in the Netherlands. *Nutr, Cycl. Agroecosys.* 50, 209-222.
- Van der Zee, S.E.A.T.M., van Riemsdijk, W.H., 1987. Transport of reactive solute in spatially variable soil systems. *Journal of water resource research* 23, 2059-2069.
- Velleman, P. F., 1980. Definition and comparison of robust nonlinear data smoothing algorithms', *Journal of the American Statistical Association*, 75, 609-615.
- Vogeler, I., Green, S.R., Clothier, B.E., Kirkham, M.B., Robinson, B.H., 2001. Contaminant transport in the root zone. in *Trace Elements in Soil: Bioavailability, Flux and Transfer*. I.K. Iskandar and M.B. Kirkham, Eds. Lewis Publishers. Boca Raton, FL, chap. 9.
- Weng, L.P., Temminghoff, E.J., Lofts, S., Tipping, E., Van Riemsdijk, W.H., 2002. Complexation with dissolved organic matter and solubility control of heavy metals in a sandy soil. *Journal of environmental science and technology*. 36, 4804-4810.

Wetterhahn, K. E., Hamilton, J.W., 1989. Molecular basis of hexavalent chromium carcinogenicity: Effect on gene expression. *Science of The Total Environment*, 86, (1–2), 113-129.

## Figures

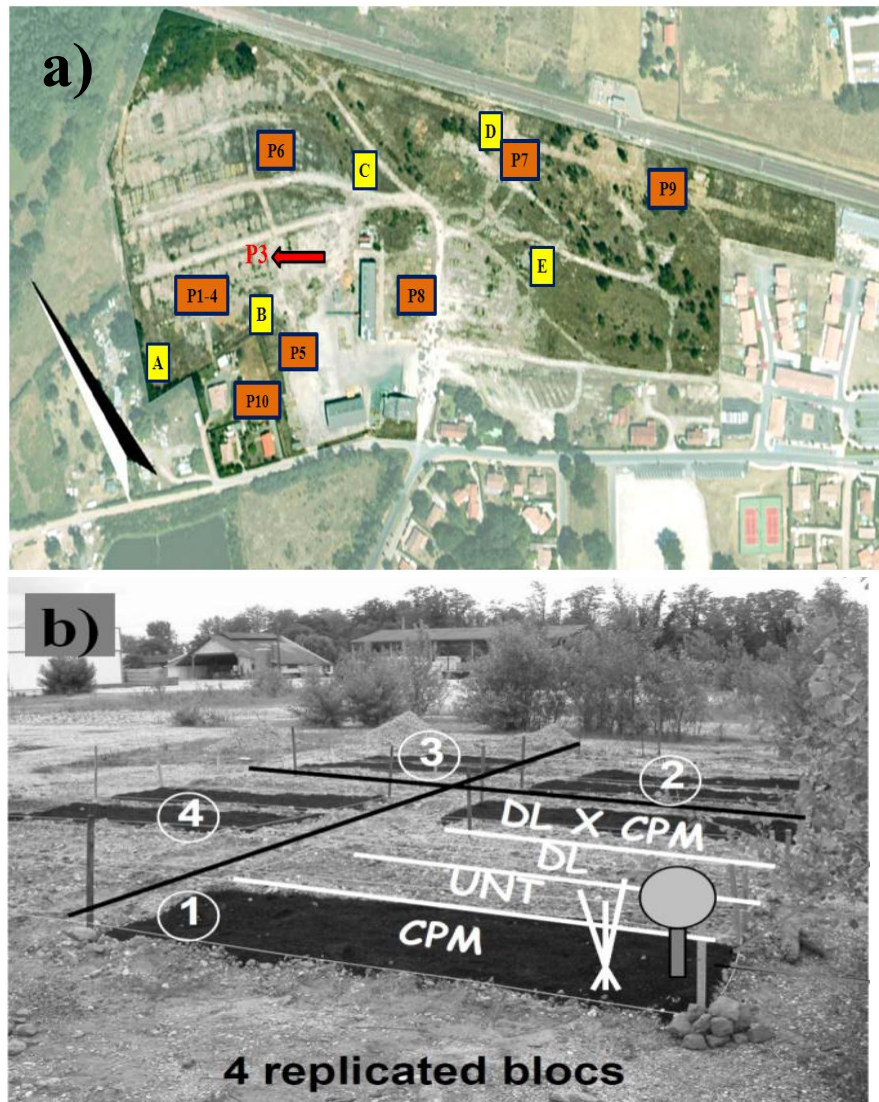


Figure1. **a)** Location of studied sites from A to E. The arrows indicate the studied site P3 (adapted from Mench and Bes, 2009)- **b)** The two plots of soil with the different types of amendment (adapted from Bes, 2008).



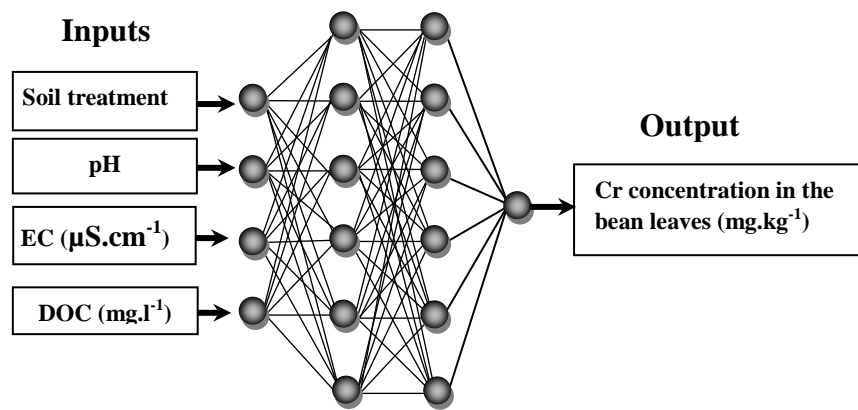


Figure 2. Neural network architecture composed of four input layers, two hidden layers and one output layer.

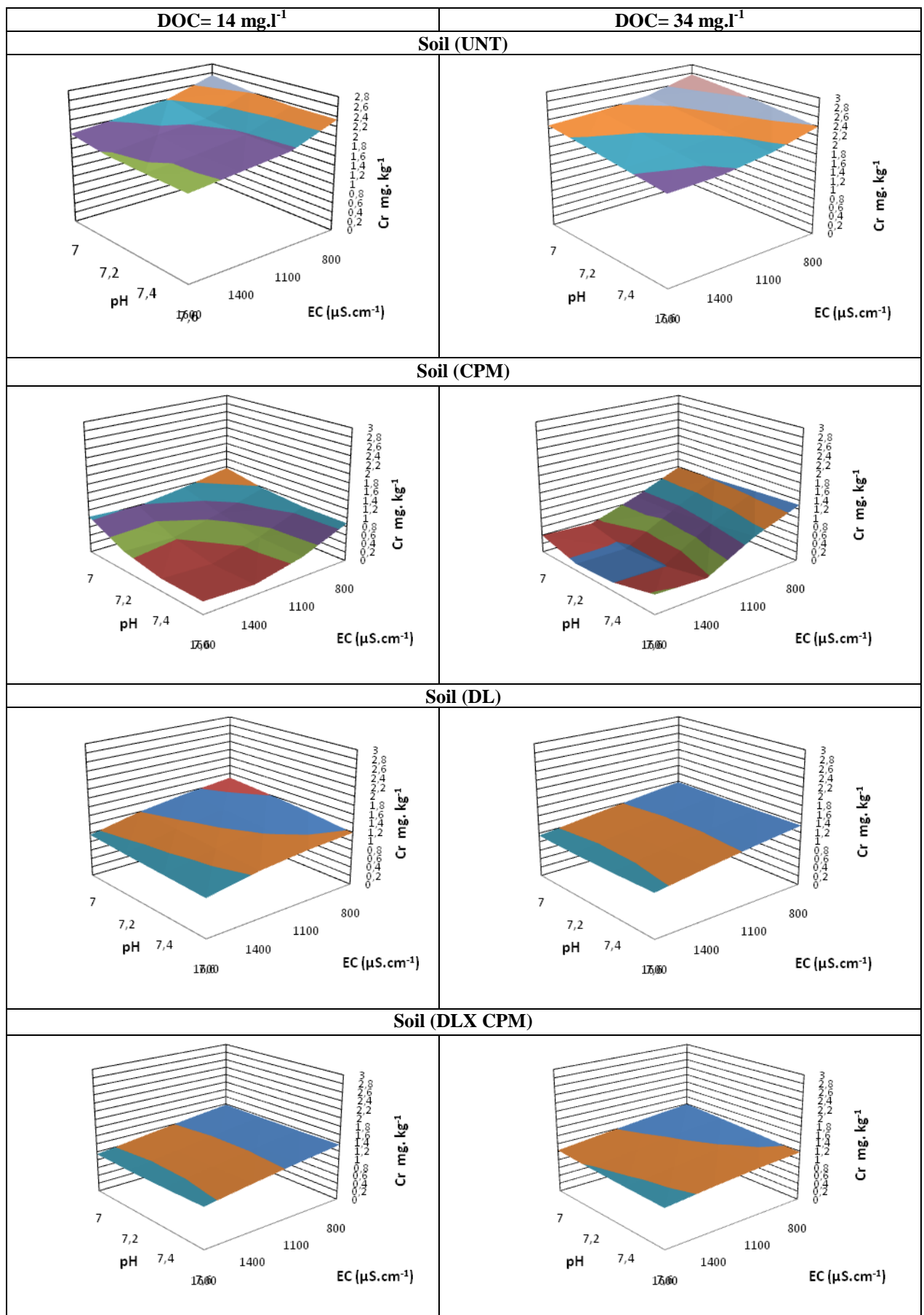


Figure 3. Chromium concentration in BL in  $\text{mg.kg}^{-1}$ : effects of soil pH and EC for two different limit values of DOC.

## The tables

Table 1. Main characteristics of site P3 (0-0.25 m soil layer).

Parameters	Site P3	Background values in French sandy soils <sup>a</sup>
<b>Sand %</b>	83.5 ± 1.1	
<b>Silt %</b>	11.5 ± 0.9	
<b>Clay %</b>	3.8 ± 1.2	
<b>C/N</b>	17.2	
<b>OM (g.kg<sup>-1</sup>)</b>	15.9	
<b>CEC (cmol<sup>+</sup>.kg<sup>-1</sup>)</b>	3.49	
<b>Organic C (g.kg<sup>-1</sup>)</b>	9.19	
<b>total N (g. kg<sup>-1</sup>)</b>	0.534	
<b>pH</b>	7.0 ± 0.23	
<b>As (mg.kg<sup>-1</sup>)</b>	9.8	1.0-25 <sup>b</sup>
<b>Co (mg.kg<sup>-1</sup>)</b>	2	1.4-6.8
<b>Cu (mg.kg<sup>-1</sup>)</b>	674 ± 126	3.2-4.8
<b>Cr (mg.kg<sup>-1</sup>)</b>	23	14.1-40.2
<b>Mn (mg.kg<sup>-1</sup>)</b>	181	72-376
<b>Ni (mg.kg<sup>-1</sup>)</b>	5	4.2-14.5
<b>Zn (mg.kg<sup>-1</sup>)</b>	46	17-48

<sup>a</sup> median and high vibrissae values except for As (Baize., 1997; Baize and Tercé, 2002). <sup>b</sup> common As mean values for all French soil types (Baize and Tercé, 2002).

Table 2. The experimental values (pH, EC, DOC and Cr). Four replications were performed for each measurement generating 64 testing results (4 soils × 4 amendments × 4 replicates) allowing for the determination of the mean values, standard deviations (SD) and coefficient of variations (COV).

Soil reference	Amendments	Mean pH	SD-COV (%)	Mean EC ( $\mu\text{S}\cdot\text{cm}^{-1}$ )	SD-COV (%)	Mean DOC ( $\text{mg}\cdot\text{l}^{-1}$ )	SD-COV (%)	Mean Cr concentration in the soil ( $\text{mg}\cdot\text{kg}^{-1}$ )	SD-COV (%)
B1-1	UNT	7.12 NS	0.15-2.08%	1114 NS	214.7-18.31%	15.93*	4.01-7.75%	15.97**	0.98-6.30%
B2-8	UNT	7.31 NS		1230 NS		14.34*		16.21**	
B3-15	UNT	7.28 NS		917 NS		21.74*		15.81**	
B4-10	UNT	6.99 NS		1430 NS		24.32*		14.07**	
B1-2	CPM	6.98 NS	0.27-3.67%	1018 NS	122-14.24%	27.08*	4.50-5.44%	14.67**	0.34-2.31%
B2-5	CPM	7.60 NS		884 NS		20.64*		15.03**	
B3-16	CPM	7.46 NS		771 NS		25.85*		15.15**	
B4-11	CPM	7.26 NS		754 NS		33.99*		14.40**	
B1-4	DL	7.49 NS	0.14-1.87%	1654 NS	308.3-24.79%	26.34*	4.14-6.96%	17.16**	0.11-0.66%
B2-7	DL	7.67 NS		1000 NS		25.76*		16.98**	
B3-14	DL	7.43 NS		1013 NS		26.52*		17.13**	
B4-9	DL	7.34 NS		1308 NS		38.46*		16.93**	
B1-3	DLX CPM	7.45 NS	0.32-4.46%	1192 NS	152.2-11.90%	33.12*	2.50-7.02%	16.09**	0.2-1.27%
B2-6	DLX CPM	7.00 NS		1347 NS		34.26*		15.91**	
B3-13	DLX CPM	7.07 NS		1457 NS		29.16*		15.93**	
B4-12	DLX CPM	7.59 NS		1119 NS		29.75*		16.35**	

\* Significant for  $p < 0.05$ , \*\* highly significant for  $p < 0.001$ , NS (non significant).

Table 3. Selected inputs and output for ANN training (UNT=#1, CPM=#2, DL=#3, DLX CPM=#4).

<b>Inputs</b>	<b>Level</b>	<b>Min value</b>	<b>Max value</b>
<b>Soil treatment</b>	4	#1	#4
<b>pH</b>	4	6.98	7.6
<b>EC (<math>\mu\text{S.cm}^{-1}</math>)</b>	4	754	1654
<b>DOC (<math>\text{mg.l}^{-1}</math>)</b>	4	14.337	34.260
<b>Output</b>			
Cr concentration in the bean leaves ( $\text{mg.kg}^{-1}$ )			

Table 4: Dry weight (g), concentration ( $\text{mg}\cdot\text{kg}^{-1}$ ) and mineral mass of Cr (g per pot) measured in the BL.

<b>Soil amendments</b>	<b>Dry Weight (g)</b>	<b>Cr concentration in the plant (<math>\text{mg}\cdot\text{kg}^{-1}</math>)</b>	<b>Mineral mass (g per pot)</b>
<b>UNT</b>	0.087 $\pm$ 0.04	1.438 $\pm$ 1.23	0.094 $\pm$ 0.03
<b>CPM</b>	0.112 $\pm$ 0.02	0.733 $\pm$ 0.08	0.083 $\pm$ 0.01
<b>DL</b>	0.122 $\pm$ 0.02	0.588 $\pm$ 0.17	0.069 $\pm$ 0.00
<b>DLX CPM</b>	0.103 $\pm$ 0.00	0.652 $\pm$ 0.012	0.067 $\pm$ 0.01

Table 5. Comparison between averaged measured and ANN predicted values of Cr concentration in the bean leaves for the four soil groups. The determination coefficient  $R^2$  is based on the eight experimental samples kept for validation.

<u>Soil (UNT)</u>		<u>Soil (CPM)</u>		<u>Soil (DL)</u>		<u>Soil (DLX CPM)</u>	
<u>Measured</u>	<u>NN</u>	<u>Measured</u>	<u>NN</u>	<u>Measured</u>	<u>NN</u>	<u>Measured</u>	<u>NN</u>
3.29	3.285	0.762	0.764	0.519	0.519	0.524	0.523
0.748	0.746	0.709	0.710	0.775	0.773	0.819	0.820
0.601	0.600	0.392	0.391	0.892	0.890	0.805	0.804
0.661	0.662	0.498	0.496	0.618	0.616	0.781	0.780
<b><math>R^2=0.9998</math></b>		<b><math>R^2=0.9986</math></b>		<b><math>R^2=0.9989</math></b>		<b><math>R^2=0.9991</math></b>	



Table 6. Selected four inputs for the ANN prediction. Full factorial combinations generate 256 ( $4 \times 4 \times 4 \times 4$ ) data to investigate their effects on soil response.

<b>Inputs</b>	<b>min</b>	<b>max</b>	<b>Level 1</b>	<b>Level 2</b>	<b>Level 3</b>	<b>Level 4</b>
<b>Soil treatment</b>	#1	#4	UNT	CPM	DL	DLX CPM
<b>pH</b>	6.98	7.6	7.0	7.2	7.4	7.6
<b>EC (<math>\mu\text{S.cm}^{-1}</math>)</b>	754	1654	800	1100	1400	1600
<b>DOC (<math>\text{mg.l}^{-1}</math>)</b>	14.337	34.260	14	20	28	34

Table 7. Correlation coefficients obtained by ANN and MLR methods.

Method	UNT		CPM		DL		DLX CPM	
	Training data	Training data	Training data	Training data	Training data	Training data	Training data	Training data
<b>Neural network</b>	0.999	0.998	0.998	0.996	0.998	0.997	0.999	0.995
<b>Linear regression</b>	0.876	0.695	0.792	0.702	0.765	0.637	0.882	0.802