Relationship of Zeta ($\zeta$) Potential with Heavy Metal Contents in Three Soil Types Management at Three Depths in Northern Mexico

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Abstract: The objective was to determine the level of zeta ($\zeta$) potential in three soil types at three depths and to analyze their relationship with physical-chemical-heavy metals variables. A factorial treatment design 3x3 was utilized. Factor A was soil management with three levels: (1) soil with a history of and still under irrigation (IS), (2) soil with an irrigation history but irrigation ceased (ISS) and (3) soil without any history of irrigation called natural soil (NS). Factor B was soil depth; 0-15, 15-30 and 30-50 cm. The $\zeta$ potential was measured in the soil's saturation extract according to Mexican Norm-021-RECNAT-2000 and evaluated with a Zetasizer 3000HSA device. The $\zeta$ potential was determined for the pH values of 1.20±0.20, 3.00±0.20, 5.00±0.20, 7.50±0.20, 9.00±0.20 and 11.00±0.20. The physical-chemical-heavy variables evaluated were: pH, electrical conductivity (EC), Organic Matter Content (OM) and the elements Na, K, Cd, Pb, Ni, Cr, Cu, Fe and B. Generally, in the three soil types and the three depths, $\zeta$ potential values increased. In IS, a cubic model was adjusted (R²=97.0%). In ISS, the soil profile from 15-30 cm depth displayed a larger variation of $\zeta$ potential with a range of -11.0 mV to -27.0 mV. Data were adjusted to the cubic model (R²=85.8%). In NS soil, $\zeta$ potential showed a similar trend to that of ISS, but the soil profile from 0-15 cm exhibited the Point Zero Charge (PZC) at a value of 1.20 cm. Data also conformed to the cubic model (R²=92.6%). The pH, EC and OM detected statistical differences for soil type but not for Factor B or the interaction. The physical-chemical-metal amounts were different for soil type management and the analysis showed a correlation of $\zeta$ potential with the EC parameter (P = 0.04), K (P = 0.03), Cd (P = 0.02) and Ni (P = 0.02).

Key words: Zeta ($\zeta$) potential • Heavy metals • Mexico • Irrigation • Natural soils

INTRODUCTION

Soil is considered an essential natural resource in supporting life on earth. Nevertheless, it has constantly experienced degradation around the world [1] due mainly to anthropogenic activities [2] becoming a potential threat to human and water safety. A virgin soil’s attributes will depend on the bedrock type from which the parent material was derived [3]. However, the man made activities may increase the amount of pollutants in soils, especially those known as heavy metals [4] which accumulate in soils in different forms [5].

Kretzschmar et al. [6] defined soil colloids as those particles ranging from >1 nm to <1 μm and it is well known that these particles are chemically very active. The colloids’ surface site may be negatively or positively charged or, in some cases, may be electrically neutral. This charge will change with the addition of other colloids coming from other sources like metals. Accordingly, to find the charged sites on a given soil, particles are essential for understanding the basic retention-adsorption processes of metals [7 and 8] and other reactions like occlusion and precipitation [9]. For instance, a low pH in soil induces desorption and dissolution of some heavy...
metals, whereas a high pH facilitates sorption and precipitation of others [10].

In Mexico's case, the soil heavy metals contamination is a high priority problem that requires immediate attention [11] because of its potential risk to human health [12,13] and the environment as a whole [14]. Once in soil, the mobility and bioavailability of these metals will depend on the physical and chemical characteristics of the soil [15] and on environmental factors [5]. The \( \zeta \) potential is an effective parameter in learning more about colloidal differences in soils and can be used to predict the electro osmotic flow. The \( \zeta \) potential is a function of charged colloidal particles at a given pH level.

An area near the city of Chihuahua in northern Mexico has traditionally produced comestible crops such as vegetables. This area has been irrigated with water from the Chuvicuar River that is a tributary of the Conchos River, in which city wastewater flows. This area has grown in terms of industry and includes a very dynamic human population. The water of the Conchos River has been contaminated to some degree with heavy metals [16-19] therefore, we hypothesized that the soil is contaminated too. To our knowledge, there is no information concerning the relationship of heavy metals in these soils with the \( \zeta \) potential. The objective of this research was to quantify the level of \( \zeta \) potential parameter changes in three soil type management at three depths and to analyze their relationship with the content of heavy metals in the soils. These results will prove important because having a \( \zeta \) potential indicator in a contaminated soil is highly recommended before attempting certain remediation procedures like electrokinetic decontamination [20].

**MATERIALS AND METHODS**

This study was conducted during 2006-07 in an area near the city of Chihuahua, Mexico, called Ejido Tabalaopa. The soil is an Orthid Aridisol with well developed pedogenic horizons and parent material is alluvial deposits. In Mexico, an Ejido is the communal farmland of a village, usually assigned in small parcels to the villagers to be farmed under a federally supported system of communal land tenure. Part of the land of this Ejido was traditionally used to grow crops such as vegetables for human consumption. This land was partly irrigated with wastewater flowing from the city of Chihuahua. However, in 1996 the crop production for human consumption was prohibited by federal regulations. Presently, the irrigated land is utilized for producing different kind of forage while some land has been abandoned.

The study area (1,090 hectares) was divided into three zones: a zone having soils with a past and present history of wastewater irrigation (Irrigated Soil or IS); a second with a history of wastewater irrigation until 2003, but no longer further irrigated (Irrigated Soil but Stopped ISS) and lastly, a soil with no history of irrigation (Natural Soil or NS). The zone division was performed using the geographic package called *Idrisi Kilimanjaro*. Then, two random samples were selected in each soil zone and with the use of Tabalaopa's stake holders, the points were properly located for further soil sampling. At each point three composite soil samples were taken from 0-15, 15-30 and 30-50 cm depths as described in Rubio *et al.* [21]. Soil was collected in plastic bags and transported to the laboratory at the College of Zootechnology and Ecology of the Autonomous University of Chihuahua. The samples were dried, ground and passed through a 0.355mm sieve to remove rocks, roots and any large particles. The samples were then stored for further analysis.

**Zeta (\( \zeta \)) Potential:** Zeta potentials were measured in saturation extracts for each soil according to the Mexican Norm (NOM-021-RECNAT-2000) technique, AS-16. A 10 g sample of soil was added to 20 ml of distilled deionized water, shaken for 10 min and after sedimentation, the supernatant liquid was discarded. In the remaining slurry, the \( \zeta \) potential for the following pH values were determined in the ranges of 1.20±pH≤11.00, 1.20±pH≤2.00, 3.00±pH≤2.00, 5.00±pH≤2.00, 7.50±pH≤2.00, 9.00±pH≤2.00 and 11.00±pH≤2.00. The pH was adjusted by adding 0.1M or 0.01M of NH\(_4\)OH solution to reach an alkaline concentration while adding 0.1M or 0.01M of HNO\(_3\) solution to attain acid concentration. The \( \zeta \) potential was measured in a Zetasizer 3000HSA at the Research Chemistry Center of the Autonomous University of the State of Hidalgo, Mexico. To test the statistical differences in zeta potential, measures of the three soil types management and three depths, an analysis of variance (ANOVA) was conducted with a \( \text{pH} = 7.5 \) under a factorial treatment design.

**Physical-chemical Variables and Heavy Metals:** The pH and EC variables were determined for a saturated paste using a standard glass electrode for pH-meter (Hanna) and a conductivity meter (Hanna). Organic matter content (OM) was analyzed following standard
methodology [22]. Soil texture was detected by the Bouyoucos method [23]. Digestion of soil samples was accomplished with aqua regia following the analysis protocol of Canada (MAP). The metal concentrations of K, Na, Cd, Pb, Ni, Cr, Cu, Fe and B were conducted using an Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) Perkin Elmer 2100. A statistical analysis was carried out on the physical, chemical and heavy metals data by using a factorial 3x3 treatment design. Factor one was soil management and three levels were considered: IS, ISS and NS. Factor two was soil depths with three levels: 0-15, 15-30 and 30-50 cm. The statistical differences were noted at a 0.05 level of significance.

RESULTS AND DISCUSSION

Zeta (ζ) Potential: Figure 1 depicts the ζ potential at three depths in the IS soil as a function of pH. A negative trend between pH levels and ζ potential values is observed. Moreover, a similar pattern and analogous values in the three depth of the soil were distinguished. In contrast for the other two soils, the variation of ζ potential due to soil depths was negligible. Determination of the so-called Point Zero Charge (PZC) occurs when the clay surface charge drops to zero at a specified pH. Ion concentration [20] was not identified because as seen in Figure 1, all particles produced negative values at all levels of pH. A cubic model with a R²=97.0% fitted these data producing the following equation: 

\[ \text{PZ} = 3.209 - 8.209 \times \text{pH} + 0.966 \times \text{pH}^2 - 0.045 \times \text{pH}^3 \]

Figure 2 shows the ζ potential at three depths in the ISS as a function of pH. It is understood that as pH increases, the level of ζ potential at the three depths becomes increasingly negative. An exception was found at pH between 5 and 7; in this case, the ζ potential level tends to stabilize at a 15-30 cm depth or even increase slightly at depths of 0-15 cm and 30-50 cm. In addition, the ζ potential at 15-30 cm depth showed a larger variation compared to the soil from other depths. The ζ potential at 15-30 cm depth ranged from 0 mV to -28.0 mV while a 30-50 depth ranged from -11.0 mV to -27.0 mV. The PZC value was reached only at 15-30 cm depth and a pH value of 1.20. These data were adjusted to a cubic model (R²=85.8%) represented in the following equation: 

\[ \text{PZ} = 6.641 - 10.69 \times \text{pH} + 1.476 \times \text{pH}^2 - 0.072 \times \text{pH}^3 \]

Figure 3 shows the ζ potential at three depths of a NS soil as a function of pH. The trend was similar to the one obtained in the ISS soil; however, the soil from 0-15 cm exhibited the PZC at a value of 1.20 cm. In this soil, the depths 0-15 and 30-50 cm revealed the larger variation when compared to the 15-30 cm. The data of this soil type were adjusted to the following cubic model (R²=92.6%): 

\[ \text{PZ} = 9.791 - 14.13 \times \text{pH} + 2.035 \times \text{pH}^2 - 0.099 \times \text{pH}^3 \]

It is important to point out that for all three types of soil management and depths, ζ potential migrated in an increasing direction (Figures 1, 2 and 3). Soil metal binding capacity change according to soil type and it is generally accepted that clay and organic soil exhibit higher metal binding than sandy soil [24]. The significance of these results is that during an electrokinetic decontamination performance, it will be necessary to keep the pH high enough to get the most negative ζ potential that will prevent the hydrolysable metal ions present in the soil from settling as metal hydroxide. Furthermore, these results can be used to estimate the diffuse layer potential and the tendency of the colloids to disperse. The ANOVA showed statistical differences for ζ potential due to the type of soil management but no differences were noted in soil depth increments and the interaction.

Heavy Metals and Physical-chemical Parameters: There was statistical differences (P<0.002) for soil type but no differences were noted for factor two or the interaction. It is well known the important role of pH in mobility and bioavailability of metals in soils. In this study, high pH values of 8.70 were found at 0-15 cm, 8.85 at 15-30 cm and 8.5 at 30-50 cm depth increments in NS soil management, while lower pH values of 7.90 at 0-15 cm, 7.95 at 15-30 cm and 7.80 at 30-50 cm were recorded in IS soils. These results concur with the findings of McLaren et al. [25] and Richards et al. [26] who observed that an application of sewage sludge to soil decreased the pH level. In the three types of management, the pH was moderately alkaline. The results of the present study are similar to those reported by Ig et al. [27] who found a decrease of pH with increasing depth but no significant differences.

The EC showed similar results than pH as soil management (P<0.001); however, no differences were noted for factor two or the interaction. These results differ from those reported by Ig et al. [27] who observed that EC values decreased with increasing soil depth. As expected, maximum EC levels were noted in IS with a mean 0.62 dS m⁻¹ a value not representing a salinity problem. The OM variable varied for soil type (P=0.004), but no differences were noted in the factor two or the interaction. The maximum amount of OM in IS (3.07%) was not unexpected since previous studies have demonstrated that the OM levels in soils increase with the application of sewage [28,29]. In fact, Antilen et al. [30] concluded that
Fig. 1: Variation of zeta potential in three soil depths with irrigation background (IS) and still irrigated as a function of pH.

Fig. 2: Variation of zeta potential in three soil depths with irrigation background but no actual irrigation (ISS) as a function of pH.

Fig. 3: Variation of zeta potential in three depths of natural soil (NS) as a function of pH.
Fig. 4: Interaction effects in three zones (soils) and three depths for sodium

Fig. 5: Correlation analysis of zeta potential as a predicting variable for electrical conductivity in a soil with a pH=7.5.

Fig. 6: Correlation analysis of zeta potential as a predicting variable for potassium in a soil with a pH=7.5.
biosolid applications represent an excellent alternative to increasing OM losses in some altered environments. These three variables: pH, EC and OM act in a synergistic way; for instance, it is known that OM applications reduce pH levels but might increase the level of EC [31]. It is crucial to point out that OM has proven to be the most essential soil component controlling the sorption and desorption of metals [32].

In this study, there was no statistical difference for the K concentration in any factor or interaction. The maximum K level in IS was 348.8 mg kg⁻¹, while in ISS was 327.2 mg kg⁻¹ and in NS was 337.4 mg kg⁻¹. A similar pattern was observed in different soil depths for this element. Laskowski et al. [33] reported that K was the only element that consistently decreased in testing four different litters under a temperate forest environment. The K values reported in this study are higher than those noted by Ilg et al. [27] who specified amounts of 84±21 mg kg⁻¹ in the upper soil profiles. Regarding the Na amount, there were statistical differences for soil type (P=0.007) and the interaction (P=0.001) but no differences were noted for depth (Figure 4). IS contains a Na concentration of 195.53 mg kg⁻¹ while the higher amount was noted in NS with 202.76 mg kg⁻¹. The Cd concentration was different for soil type (P=0.003) but no differences were noted for soil profile or the interaction. The maximum level of these elements was noted in IS with 4.66 mg kg⁻¹ in relation to 3.69 mg kg⁻¹ in ISS and 1.64 mg kg⁻¹ in NS. This metal is considered mobile in the soil profile, e.g. research has shown annual losses as high as 0.27 and 0.86 g Cd ha⁻¹ in New Zealand’s fertilized soils [34] and leaching of Cd increased with sewage sludge applications [25]. The Cd amount in the three soils tested in this research was higher than values reported in a soil in India, which was within the range of 0.032 mg kg⁻¹ to 0.036 mg kg⁻¹ [35].

Lead concentration was not different for any factor or the interaction. This metal is a relatively immobile element in soil. McLaren et al. [25] found small amounts of Pb leached after heavy applications of sludge. In another study, Kumar et al. [35] noted a range of Pb concentration in a soil in India of 15.8 to 18.9 mg kg⁻¹ which is lower than the results of the present study, where Pb was noted in a range of 63.54 mg kg⁻¹ to 65.84 mg kg⁻¹. There were differences for Ni concentration (P=0.015) due to soil type, but no differences were noted for depth or the interaction. Maximum amount of Ni was detected in IS with 12.40 mg kg⁻¹ while a lower level was noted in NS with 7.13 mg kg⁻¹. This element is mobile in soil because it has been found in groundwater wells at a pasture site treated with sewage sludge [36 and 37]. With respect to Cr levels, there were differences only for soil type (P=0.033) observing the highest amount in NS with a value of 42.28 mg kg⁻¹. This result was surprising because the original hypothesis was that the content of this element would be greater in IS than in the other two soils tested, but it is well documented that this metal is less mobile in soils than other metals [25, 38].

There were statistical differences for Cu levels due to soil type with a maximum concentration in IS of 20.87 mg kg⁻¹ when compared to levels of 6.21 mg kg⁻¹ in ISS and 7.73 mg kg⁻¹ in NS. The Cu level in ISS may be explained by the leaching process of this element because like Ni, it is mobile in soil and after ceasing irrigation, it could move to other zone [36, 37]. The Cu concentration of 20.87 mg kg⁻¹ is similar to a soil in India as Kumar et al. [35] reported a Cu amount within the range of 19.0 to 23.4 mg kg⁻¹. A similar pattern was noted for Fe and B concentrations, where there were differences due to soil type (P=0.019) but no differences in factor two or the interaction. The highest amount of Fe was found in IS with a value of 18.576 mg kg⁻¹. Factor two was different only due to factor one. The maximum amount was noted in ISS with 87.34 mg kg⁻¹ when compared to the lower amount observed in NS with 15.81 mg kg⁻¹.

Zeta (ζ) Potential Correlations: The correlation analysis carried out for the physical-chemical variables tested in this study with the ζ potential variable, showed that the ζ potential was only statistically correlated with the EC (P=0.04). The model obtained that fit the data was cubic and is suitably represented in Figure 5. The correlation analysis was performed using a pH=7.5 and applying the following model; EC=10.68 + 1.660ζ p + 0.085ζ p² + 0.001ζ p³. Regarding the correlation analysis of the metals tested with the zeta potential, a statistical correlation was found for K (P=0.03), Cd (P=0.02) and Ni (P=0.02). The correlation model for K- ζ potential was cubic (Figure 6) and the best fitted model was: K=1094 + 120.5ζ p + 6.10ζ p² + 0.098ζ p³. The one for Cd- ζ potential was cubic (Figure 7) and the model obtained was Cd = -198.4 + 28.80ζ p + 1.380ζ p² + 0.021ζ p³. Finally, the best equation for Ni- ζ potential was quadratic (Figure 8) and the model was Ni = -36.85 - 4.021ζ p - 0.080ζ p². In the correlation graphs, it is clear that ζ potential values are the most negative. The values of the other variables have a tendency to decrease, as seen in the EC graph; note the range of ζ potential from -20.0 to -15.0 mV. The values of EC are close to 0.3 dSm⁻¹ when compared to ζ potential values that are lower than -20.0. All the EC points are for above the 0.4 dSm⁻¹.
CONCLUSIONS

These results highlight the importance of understanding the relationships among the heavy metals contents of three soils with $\zeta$ potential values. This is important because most of the studies that try to understand the electrokinetic properties of the soil’s particles have been performed using pure minerals. But, in this particular case, we dealt with heterogeneous types of soils and basic information and data is presented. The average concentrations of heavy metals in these three soils agree with values reported in a worldwide basis. Our findings are relevant because we found that in the three soil types as well as in the three depths, the $\zeta$ potential migrated in an increasing direction.

REFERENCES


