

Soil Quality Evaluation of Hydrocarbon Polluted Parcels

Margarita Teutli León, Marco Antonio Cruz Gómez, José Castillo Román, Andrés Sánchez

Engineering Department, Benemérita Universidad Autónoma de Puebla (BUAP), Puebla, México

Email: maria.teutli@correo.buap.mx, mteutlileon@gmail.com

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Abstract

For hydrocarbon polluted soils that underwent bioremediation it is important to assess its condition after a period of time, but it is more useful when there is an opportunity of comparison against an unpolluted soil and an untreated polluted one. This paper provides a comparison of three adjacent parcels, being the first clean, the second polluted and bioremediated, the third polluted and left to natural attenuation. Study was conducted determining pH, electrical conductivity, carbonates, soil organic matter, chemical oxygen demand, eight anions, and twelve metals. Data were compared against those references for agricultural soils found in the Mexican NOM-021. A Pearson correlation was applied to find coincidences between the three parcels, obtained results allowed to say that bioremediated parcel allowed for most uniform pH, negligible salinity risk, and medium content of soil organic matter, but treatment has enabled heavy metal accumulation since its values are higher in respect to the other parcels. Natural attenuated parcel has some spots with lower pH, a moderately saline risk, a high content of soil organic matter, and lower content of heavy metals. The clean or unaffected parcel exhibit the higher pH values, a slightly saline condition, soil organic matter ranges from high to very high content, heavy metals content is medium, but no reaching dangerous levels. An important assessment is that bioremediation has enhanced the bio-availability of soil organic matter but it is not similar to the values in the unpolluted parcel.

Keywords

Soil Quality, Hydrocarbon Pollution, Soil Unpolluted, Bioremediation, Natural Attenuation

1. Introduction

Hydrocarbon (HC) polluted soils remediation have been approached accounting

for soil properties, ionic content as well as amendments addition, these methods have covered a wide variety of reagents being either chemical or natural products.

It is widely accepted that a remarkable proportion of Hydrophobic Organic Compounds (HOCs) once they enter into the soil will tightly associate with soil aggregates and persist in them.

It has been reported that soil concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) exhibit dependence on both surface area and bulk chemical composition of organic matter, especially those associated to humic substances (Chen et al., 2017). Presence of PAHs in soils can be originated from natural and anthropogenic sources. PAHs entering the soil can be degraded by biological and physicochemical processes; the rate at which these processes occur and the degree in degradation or retention is controlled by factors like: soil properties, soil type, microbiological content and PAHs physicochemical properties; although the major processes by which PAHs become lowered in concentration are the biotic ones.

In terms of soil remediation there have been two main trends: one focuses on pollutant removal and other for reduction of mobility and/or bioavailability of pollutants, some authors pointed out that the purpose of remediation goals should clearly account for the terms recultivation, rehabilitation, restoration and reclamation, when defining the goals pursued in soil decontamination; in this sense, presence of metals in organic systems should be considered as part of the solution for soil remediation (Floris et al., 2017). Metal interactions should be studied at deep levels, because reaction mechanisms are not clearly understood; for instance, an adsorbent that acts like metal sink reduce bioavailability of some metals but also it can behave like a reducing agent acting onto carbon-halogen bounds.

The effectiveness of plant-bacteria partnerships depend largely on the survival and metabolic activities of exogenous bacteria carrying degradation genes, which are required for the enzymatic degradation of organic pollutants, then HC can be degraded if there is a plant bacteria association where the bacteria is having both characteristics: pollutant degrading and enhancement of plant growth activities; in this sense, the most beneficial bacteria are those living in the root zone (Khan et al., 2013).

Biodegradation of organic contaminants in soil is a complex problem involving factors like organic matter content, clay fraction, temperature, water content, pH, presence of ions like Na^+ , Cl^- , CO_3^{2-} , SO_4^{2-} , particle size, porosity distribution, oxygen supply and the C/N ratio. It has been observed that salinity impede rapid removal of hydrocarbons from soil as far as microbial activity is inhibited, but addition of wastewater sludge might alter soil characteristics and provide nutrients and microorganisms to accelerate their dissipation. For instance, in two soils amended with wastewater sludge and polyacrylamide it was obtained a faster removal of anthracene and phenanthrene (Fernández-Luqueño et al., 2016). A study of three oil spillage sites, in which samples were amended with poultry

manure authors reported getting up to 40% removals using a 25% amendment (Ezene et al., 2014).

There is a dual effect of compost addition onto the organic pollutants (Ops) bioavailability because it can occur either one of three scenarios: 1) stimulation of native microorganisms by compost nutrients and organic matter, as well as enhancement of microbial activity by introduced compost microorganisms; 2) introduction of organic matter will increase adsorption of Ops; 3) an increase of Dissolved Organic Matter (DOM) favors solubility and desorption of OPs improving the uptake by soil microorganisms. Therefore, it is important to monitor OPs bioavailability and the proper compost/soil ratio in order to get the highest microbial activity enhancement (Ren et al., 2018).

A field study to evaluate ecological effects of petroleum contamination on soil biological activity was done using bioremediation by bioaugmentation and bio stimulation, results were compared with natural attenuation (Polyak et al., 2018), degradation of Total Petroleum Hydrocarbons (TPHs) were determined, as well as soil basal respiration and enzyme activities, the last is a sensitive indicator of environmental pollution.

Anaerobic degradation of organic pollutants is highly dependent on the supply of electron receptors like nitrate (NO_3^-), sulfate (SO_4^{2-}) and metal oxides. It is known that some microorganisms can degrade PAHs under anaerobic conditions, but few of them are able to do it in natural conditions, because there is a lack of appropriate electron receptors, an option has been using the Microbial Fuel Cell (MFC) (Yu et al., 2017) a device which generates electricity by microbial catabolism of either organic/inorganic substrates improving electron transfer because it contains a non-soluble receptor.

Since available techniques for *in-situ* and *ex-situ* remediation can be prohibitively expensive, the Risk Based Land Management can be an option for sustainable management of contaminated land; usually there is an imbalance between remediation actions and the involved waste generation; in this scheme two key decisions are the time frame and the washing solution. Current trends for soil remediation techniques consider this preferential sequence: bioremediation > integrated techniques (physical/chemical/biological) > chemical > oxidation > solvent-extraction > heating > electrokinetic remediation (Kuppusamy et al., 2017a, 2017b).

For polluted soils that underwent bioremediation it is important to assess soil condition after long time, in this sense it was found a place with landfarming activities which was subject of HC spill, due to soil slope the HC run-off affected 2 parcels and left one unaffected. From the two affected due to economical restrictions only one was bioremediated and the other one was left to natural attenuation. Therefore, this site was considered ideal to assess the usefulness of bioremediation, since there is the opportunity to compare with the one left to natural attenuation and the condition of the unpolluted one.

For landfarming use, it is required to assess soil quality, and evaluation should be based on soil physical chemical parameters (USDA, 2015), including those

referred by the Mexican norm NOM-021 (Gobernación, 2011). Useful parameters are described in the following section.

2. Important Parameters for Soil Quality Characterization

2.1. Soil Electrical Conductivity (EC, $\text{dS}\cdot\text{m}^{-1}$)

It is a measure of the amount of salts in soil, it can act as an indirect indicator for soluble nutrients. Saline condition affects microbial activity impacting essential soil processes like respiration, residue decomposition, nitrification and denitrification processes (USDA, 2015). According to the NOM-021 EC values can be used for soil salinity risk estimation. According to NOM-021 salinity risk can be negligible effects ($\text{EC} < 1.0$), very slightly saline ($1.1 < \text{EC} < 2.0$), moderately saline ($2.1 < \text{EC} < 4$), saline ($4.1 < \text{EC} < 8$), strongly saline ($8.1 < \text{EC} < 16$) and very strongly saline ($16 < \text{EC}$)

2.2. Soil Sodium Adsorption Ratio (SAR)

This parameter indicates the soil sodification risk. It is a measure of the amount of Na relative to Ca and Mg, and it is calculated by the equation:

$$\text{SAR} = [\text{Na}] / \left(\sqrt{([\text{Ca}] + [\text{Mg}]) / 2} \right) \quad (1)$$

Concentration of Na, Ca, Mg should be in millimoles per liter or milliequivalents per liter. Reference quality values were found in standards for irrigation water (Burger & Celkova, 2003) being low risk ($\text{SAR} < 10$), hazard for fine texture soil having high cation exchange capacity ($10 < \text{SAR} < 18$), high risk ($18 < \text{SAR} < 26$) specially this case requires a special soil management, very high risk ($26 < \text{SAR}$) water is unsuitable for irrigation purpose.

2.3. Soil Organic Matter (SOM, %)

Total Organic Carbon (TOC) is that stored in the SOM, for soils this is the organic fraction of non-decomposed plant and animal residues, it is a heterogeneous dynamic substance that varies in particle size, carbon content, decomposition rate and turnover time. SOM it is the most important indicator of soil health since its presence defines biological control of plant diseases and pests (USDA, 2015). It is a key factor for soil functions like nutrient supply, available water capacity, soil aggregation, erosion, soil carbon retention. For non-volcanic soils the NOM-021 indicates that SOM classifies as very low ($< 0.5\%$); low ($0.6\% < \text{SOM} < 1.5\%$), medium ($1.6\% < \text{SOM} < 3.5\%$), high ($3.6\% < \text{SOM} < 6\%$), and very high ($6\% < \text{SOM}$).

2.4. Soil Chemical Oxygen Demand (COD, $\text{mg}\cdot\text{kg}^{-1}$)

This parameter implies an indirect measure of the decomposability for organic matter soluble compounds. A method (Kolar et al., 2003) using 5% soil suspension to determine COD by the traditional dichromate method, and the Biochemical Oxygen Demand (BOD_5), it was found that there is a first order kinetic

ics between BOD₅ and COD. There are not reference values.

2.5. Soil Nitrate Content (NO₃, mg·kg⁻¹)

Nitrate is an excellent indicator of soil organic matter mineralization, used as indicator of nitrogen (N) cycling, it helps to determine if the crops use the nitrogen or if there is need to supply additional amounts through fertilizers (USDA, 2015). A concentration of 20 mg·l⁻¹ in the surface layer is adequate for high demanding N crops like corn, but 40 mg·l⁻¹ or more restricts the ability of bacteria and legumes to fix N. It is reported that soil pH < 5.5 reduces nitrification, optimum range is 6 < pH < 8. Otherwise high NO₃ concentrations can lead to pollution of surface and groundwater, as well as they represent a high risk of eutrophication.

2.6. Soil Phosphorus (P, Determined as PO₄³⁻, mg·kg⁻¹)

This parameter is one of the most limiting nutrients for crops and forage; its availability is highly related to soil pH and electrical conductivity. Best pH for phosphorus bioavailability is in the range of 6.0 - 7.5, out of this range it can be favored phosphorus fixation by Fe, Al or Ca (USDA, 2015), measurement in soil is done through phosphate (PO₄) determination. The NOM-021 considers P content categories as low (<5.5 mg·Kg⁻¹), medium (5.5 - 11 mg·Kg⁻¹), and high (>11 mg·Kg⁻¹).

2.7. Soil Micronutrients (Fe, Cu, Zn, Mn; mg·Kg⁻¹)

In the NOM-021 are considered Fe, Cu, Zn, and Mn. These elements have an important role in oxidation-reduction processes, formation of oxidase enzymes as well as chlorophyll formation. In the NOM-021 Fe and Zn are referred in three categories deficient (Fe < 2.5, Zn < 0.5 mg·Kg⁻¹) marginal (2.5 < Fe < 4.5, 0.5 < Zn < 1 mg·Kg⁻¹), adequate (Fe > 4.5, Zn > 1.0 mg·Kg⁻¹), while Cu and Mn have only two categories: deficient (Cu < 0.2, Mn < 1.0 mg·Kg⁻¹), and adequate (Cu > 0.2, Mn > 1 mg·Kg⁻¹).

2.8. Soil pH (Dimensionless)

This is an excellent indicator for soil suitability to enhance plant growth (USDA, 2015). For most crops optimal pH is between 6.0 - 7.5; soil below 5.5 and between 7.5 - 8.5 limits the availability of phosphate for plants, as well as N cycling is inhibited at low pH, also solubility of metals is highly dependent on pH. In the NOM-021 pH categories are defined as: strongly acid (pH < 5.0), moderately acid (5.1 < pH < 6.5), neutral (6.6 - 7.3), moderately alkaline (7.4 - 8.5), strongly alkaline (>8.5).

2.9. Soil Carbonate (CaCO₃²⁻, %)

Their reactions exert a buffering effect onto reaction leading to acidification, also this anion inhibits the heavy metal transference from soil to plants. A study

about Ni, Cd accumulation in wheat (Wang et al., 2015) reports that when carbonate is depleted in soils (<1%) Ni and Cd concentrations are about 2 - 3 times the ones found in soils having carbonate (>1%). In the NOM-021 using the Horton-Newson procedure reference values for concentration correspond to very low (<0.5% CaCO₃), low (0.6% - 2.0% CaCO₃), medium (2.2% - 15% CaCO₃), high (17% - 40% CaCO₃), very high (CaCO₃ > 40%).

2.10. Soil Heavy Metals (Cd, Ni, Pb; mg·Kg⁻¹)

It is known the high toxicity and side effects that these metals produce, therefore it is important to quantify them in order to set a risk warning if their presence exceed the threshold values (USDA, 2015). In the NOM-021, for a soil being used to grow crops there are two categories normal ($0 < \text{Cd} < 0.35$; $\text{Pb} < 35$ and $\text{Ni} < 50 \text{ mg}\cdot\text{Kg}^{-1}$), and the dangerous if ($3 < \text{Cd} < 5$; $100 < \text{Pb} < 300$, $\text{Ni} > 100 \text{ mg}\cdot\text{Kg}^{-1}$).

Based on these standards in this paper are presented results for the chemical evaluation of three adjacent parcels: one unaffected and two affected by a hydrocarbon spill, from these one of the last mentioned was bioremediated and the other was left to natural attenuation. Chemical characterization was done three years after the hydrocarbon spill took place.

3. Methodology

An aerial view is shown in **Figure 1**, parcels object of this study are located inside a polygon in red lines is described by the UTM coordinates going from point A (630112 E, 2097414 N) to point B (630457 E, 2097213 N), A and B are indicated by yellow markers. For nomenclature it was chosen to assign A = polluted parcel, insight yellow polygon, none treatment applied, it was left to remediate under natural attenuation (12 samples); B = clean parcel, inside blue polygon (12

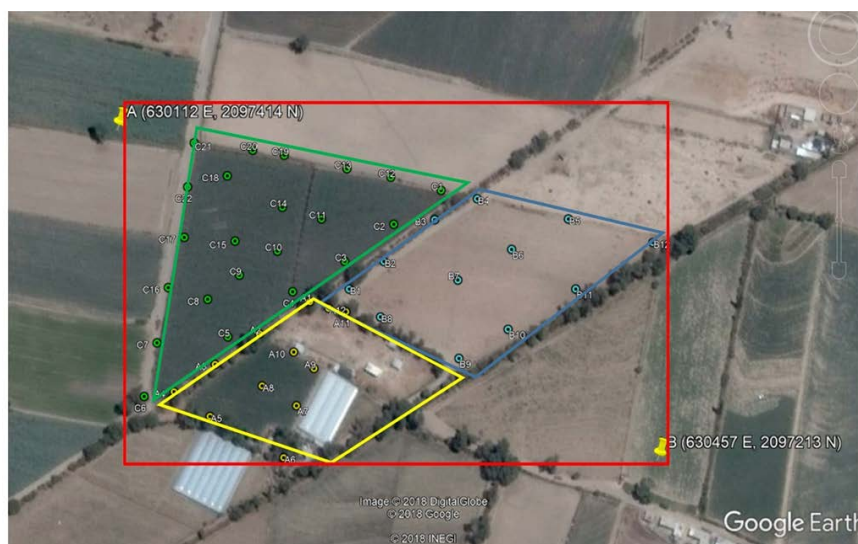


Figure 1. Aerial view of the three parcels located inside the polygon (red), parcel A (yellow), parcel B (blue), parcel C (green).

samples) and C = polluted parcel that underwent bioremediation, inside green polygon (22 samples).

Soil samples collection and analysis was done according to the Mexican NOM-021 specifications to evaluate fertility, salinity and soil classification, studies, sampling and analysis. All collected samples belong to the top soil (10 - 20 cm depth), properly labeled they were taken to the laboratory. Once there, all samples were air dried, and the analytical solutions for analysis were prepared using a 1:2 (w:v) ratio; also a water extract was obtained from a saturated soil paste.

The analytical sample was used to determine pH with a Conductronic potentiometer, Electrical Conductivity (EC, $\mu\text{S}\cdot\text{cm}^{-1}$) was measured with a CL8 Conductronic tester; anions like SO_4 , NO_3 , PO_4 , and the Chemical Oxygen Demand (COD) were determined using HACH reagents and the DR 2500 HACH spectrophotometer. Also, gravimetric methods were applied to determine chloride (Cl), phenolphthalein and methyl orange alkalinity (AlkF, AlkT), total hardness (TH), and Soil Organic Matter (SOM). Otherwise, soluble metals like Cr, Na, K, Ca, Fe, Mn, Pb, Ni, Cu, Cd, Zn, were determined by atomic absorption spectrophotometry using the GBC 932 atomic absorption spectrophotometer.

After obtaining the analytical data, using the statistical package Minitab v.17 it was applied a Pearson correlation for assessing how the chemical parameters are related between them. Considering that the correlating values are in the range from -1.0 to $+1.0$, the absolute values ranges from 0.0 - 1.0 , and values closer to 1.0 means a strongest correlation. In order to get an easier way of comparison it was set up 5 intervals between 0.0 to 1.0 ; then a very weak relationship corresponds to the interval 0.0 - 0.19 ; the weak correlation to 0.2 - 0.39 ; the moderate to 0.4 - 0.59 ; the strong to 0.6 - 0.79 and the very strong to 0.8 - 1.0 .

4. Results and Discussion

Table 1 reported the minimum (min) average (mean) and maximum (max) values for all physicochemical parameters determined in each sample from each parcel.

4.1. Salinity Risk

Evaluation based on the EC values is reported in **Table 2**, data are expressed in percentage since the number of samples is different for each parcel (12 in A, 12 in B, and 22 in C).

It can be observed that bioremediated parcel (C) exhibits a negligible risk, while the one under natural attenuation (A) has values mainly negligible but a total of 33% fall in the categories of slightly and moderately saline, otherwise the clean parcel (B) has a similar coverage in the negligible and slightly saline categories. From the analysis of EC data, it is concluded that all parcels do not overcome the slightly saline risk, but from higher to lower values the parcels can be classified as $B > A > C$.

Table 1. Physicochemical parameters of parcels A, B, C.

	Parcel A			Parcel B			Parcel C		
	min	mean	max	min	mean	max	min	mean	max
pH	7.0	8.0	9.0	8.0	8.2	8.6	7.8	8.1	8.4
E.C. uS/cm	374.0	1018.0	2630.0	632.0	957.0	1255.0	273.0	575.7	1073.0
SO ₄ , mg/Kg	0.0	86.0	360.0	0.0	85.0	360.0	0.0	55.4	600
NO ₃ , mg/Kg	6.0	56.0	252.0	18	34.6	66.0	0.0	52.0	390.0
NO ₂ , mg/Kg	0.0	56.0	100.0	40.0	102.0	200.0	0.0	188.0	1800.0
PO ₄ , mg/Kg	0.2	16.0	36.0	13.2	20.6	32.6	3.0	7.8	13.4
Cl, mg/Kg	50.0	186.0	790.0	100.0	202.4	340.0	0.0	46.4	140.0
Alkf, mg/Kg	0.0	108.0	180.0	100.0	163.0	280.0	40.0	97.2	460.0
AlkT, mg/Kg	380.0	788.0	1060.0	640.0	920.0	1220.0	460.0	618.0	920.0
TH, mg/Kg	308.0	784.0	1144.0	440.0	674.0	924.0	352.0	594.0	1144.0
COD, mg/Kg	32.0	198.0	552.0	40.0	470.0	1336.0	32.0	323.0	978.0
CO ₃ , %	0.0	0.2	2.8	0.0	1.4	5.6	0.0	3.0	8.3
SOM, %	4.4	9.0	23.5	4.4	6.6	9.7	0	2.18	6.19
Cr, mg/Kg	12.0	18.0	24.0	24.6	29.4	34.0	34.6	41.8	49.0
Na, mg/Kg	24.0	102.0	238.0	84.0	172.0	300.0	72.0	105.0	140.0
K, mg/Kg	44.0	74.0	180.0	56.0	94.0	144.0	42.0	71.0	136.0
Mg, mg/Kg	30.0	80.0	136.0	42.0	64.0	102.0	66.0	86.6	116.0
Ca, mg/Kg	112.0	196.0	312.0	40.0	72.0	116.0	60.0	102.0	352.0
Fe, mg/Kg	0.0	0.1	0.2	0.0	0.2	2.2	0.0	0.8	4.2
Mn, mg/Kg	0.0	0.3	1.5	0.1	0.2	0.4	0.0	0.4	0.6
Pb, mg/Kg	0.0	0.0	0.0	0.0	0.1	0.5	0.0	0.6	1.4
Ni, mg/Kg	1.4	2.0	3.7	2.8	3.8	5.0	4.6	6.6	8.0
Cu, mg/Kg	1.2	2.2	3.2	3.2	4.2	5.2	5.2	6.8	8.2
Cd, mg/Kg	0.1	0.2	1.1	0.2	0.4	0.6	0.6	0.4	1.0
Zn, mg/Kg	0.0	0.0	0.1	0.1	0.2	0.3	7.8	8.1	8.4

Table 2. Salinity risk as function of EC values.

Parcel	Salinity risk categories					
	Negligible	Slightly	Moderately	Saline	Strongly	Very strongly
	EC < 1, dS·m ⁻¹	1.1 < EC < 2.0 dS·m ⁻¹	2.1 < EC < 4.0 dS·m ⁻¹	4.1 < EC < 8.0 dS·m ⁻¹	8.1 < EC < 16 dS·m ⁻¹	16 < EC, dS·m ⁻¹
A	67%	25%	8%	-	-	-
B	58%	42%	-	-	-	-
C	91%	9%	-	-	-	-

4.2. Sodium Adsorption Ratio (SAR)

Using analytical data of Na, Ca, and Mg, and Equation (1) the SAR values were calculated, results quoted as minimum (min), average (mean) and maximum (max) are shown in **Table 3**. As it can be observed all SAR values are under 10 which is the threshold value to declare the sodification risk, It is noticeable that although the clean parcel (B) is the one with highest values, the difference between minimum and maximum values is lower (2.39) than the difference exhibited by the natural attenuated parcel (A) (2.70); and the bioremediated parcel (C) is the one with minimal difference (1.17); these behavior can be interpreted like a most uniform soluble ionic Na distribution is taking place in it.

The sodicity risk represented by SAR is low for all parcels, but from higher to lower SAR values parcels follow the order $B > C > A$, then the B parcel has the higher values in salinity and sodicity risk, but the bioremediated C, and the natural attenuated A exchange places when they go from salinity to sodicity risk.

4.3. Soil Organic Matter (SOM)

This is an important parameter for soil edaphic functions take place. Analytical results were compared with the threshold values for the five categories defined in the NOM-021, in **Table 4** is reported the % of samples which fall in each category. From the **Table 4** it can be observed that bioremediated parcel (C) has values spread over all categories with the main presence in the medium content category. Parcels A and B has values in the high and very high content categories, but the natural attenuated (A) has 75% of its samples in the Very High content, while the clean one (B) has similar amounts for both categories.

4.4. Chemical Oxygen Demand (COD)

The COD is a physicochemical parameter which indicates the decomposability of the organic matter, results are reported as minimum, mean and maximum in **Table 5**. It is observed that higher values belong to the clean parcel (B) which

Table 3. Sodification risk as function of SAR values.

	min	mean	max	Sodification Risk	Extremes difference
Parcel A	0.25	1.15	2.95	<10, Low risk	2.70
Parcel B	1.26	2.52	4.65	<10, Low risk	2.39
Parcel C	0.68	1.33	1.85	<10, Low risk	1.17

Table 4. Soil organic matter (SOM) categories.

	Very low	Low	Medium	High	Very High
[SOM], %	<0.5	0.6 - 1.5	1.6 - 3.5	3.6 - 6	>6
Parcel A	-	-	-	25%	75%
Parcel B	-	-	-	42%	58%
Parcel C	4.5 %	9.1%	54.5%	27.3%	4.5%

Table 5. Soil chemical oxygen demand (COD) values.

[COD], mg·Kg ⁻¹	minimum	mean	maximum	Extremes difference
Parcel A	32	178	552	520
Parcel B	40	469	1336	1296
Parcel C	32	308	968	936

means that the SOM with similar content in the category High and Very High it is highly decomposable; also based on the COD mean values it is observed that decomposability of SOM in B is 1.5 times the decomposability of SOM in C, and this is 1.7 times the decomposability of SOM in A, therefore although A has SOM content in the high and very high content, it has lower decomposability than the SOM in the bioremediated parcel. This implies that bioremediation has helped in making available the SOM, but it has not been enough to reach the values exhibited by the unpolluted parcel B.

Based on SOM parcels can be ordered as $A > B > C$, but based on COD the order switches to $B > C > A$, therefore even though A has the higher SOM, it exhibits the lower decomposability rate.

4.5. Nitrate Content Categories (NO₃)

The NO₃ results classification is reported in **Table 6**. It can be observed that polluted parcels A and C have an important presence (16.7%) in the high concentration range, while the clean one B has values in the low and adequate categories. Because acidic soils (pH < 5.5) reduce nitrification, in this sense is good that pH in the 3 parcels is higher than 7 (see **Table 1**). For all parcels more than 50% of samples lie in the low content category, but it is observed that A and B have similar percentage in the adequate range, while B and C have 16.7% in the high content, this amount is not negligible if it is accounted that this condition restricts bacteria ability to fix N.

4.6. Phosphorus Content Categories (P)

Phosphorus content is a key component for crop production results are reported in **Table 7**. As it can be observed the bioremediated parcel (C) has values in the low content, the clean parcel (B) has values in the low and medium content, and natural attenuated (A) is mainly in the low content, but values in the medium and high content cannot be negligible. Also considering that the best pH for bioavailability of P is in the range 6.0 - 7.5, the observed pH of the three parcels (**Table 1**) is about 8, this is a limiting factor. Also, P can be fixed by Fe or Ca, considering Fe content parcels follow the order $A < B < C$, while Ca defines the order $B < C < A$. These three components can be a key factor in defining the bioavailability for soluble P.

4.7. Micronutrients Fe, Cu, Zn, Mn

About micronutrients there is a coincidence in Fe and Zn, both fall in the mainly

Table 6. Nitrate (NO₃) content categories.

	low	adequate	high
[NO ₃], mg·Kg ⁻¹	<20	20	>40
Parcel A	58.3%	25%	16.7%
Parcel B	75%	25%	-
Parcel C	75%	8.3%	16.7%

Table 7. Phosphorus (P) content categories.

	low	Medium	High
[P]	<5.5 mg·Kg ⁻¹	5.5 - 11 mg·Kg ⁻¹	>11 mg·Kg ⁻¹
Parcel A	58%	25%	17%
Parcel B	33%	67%	-
Parcel C	100%	-	-

deficient criteria being 100% in parcels A and B, while C has 86% in the deficient and 14% in the marginal range. Cu exhibit a homogeneous trend since all samples have values in the adequate content which corresponds to concentration > 0.2 mg·Kg⁻¹; Mn also has uniform values falling in the deficient category for the three parcels.

4.8. pH Categories

In this parameter the three parcels exhibit mainly a moderately alkaline condition, but parcels A and B have 8% of the samples in the strongly alkaline condition. Results are shown in **Table 8**, as it was mentioned in previous paragraphs the fact that pH in the alkaline condition limits the phosphorus bioavailability, but could be good for the nitrification process.

4.9. Carbonate (CO₃) Categories

Mineral carbonates determined by CO₂ evolution are reported in **Table 9**, results are dissimilar since samples of the clean parcel (B) classify in very low content, although the amount in the medium content is significant; the natural attenuated (A) has values in the very low and the amount in the medium content is < 10% so it can be considered negligible; finally the bioremediated parcel (C) has similar amounts in the very low and the medium content; from these data it can be concluded that carbonate presence is not a determining factor for the alkaline pH.

Alkalinity is the neutralizing capacity of water due to the concentration of soluble species such as carbonates (CO₃²⁻), bicarbonates (HCO₃⁻) and hydroxides (OH⁻). According to the water relationships if $AlkF < AlkT/2$, then water alkalinity is mainly due to bicarbonate; from data in **Table 1** it can be assessed that this fact is true for the three parcels and the pH measured in the analytical solutions can be due mainly to the soluble bicarbonate, and not to the presence of mineral carbonate.

Table 8. pH categories.

Category	Strongly acid	Moderately acid	Neutral	Moderately alkaline	Strongly alkaline
pH values	<5	5.1 - 6.5	6.6 - 7.3	7.4 - 8.5	>8.5
Parcel A	-	-	-	92%	8%
Parcel B	-	-	-	92%	8%
Parcel C	-	-	-	100%	-

Table 9. Carbonate content (CO₃) categories.

	Very low	Low	Medium	High	Very High
[CO ₃]	<0.5%	0.6% - 2.0%	2.2% - 15%	17% - 40%	>40%
Parcel A	92%	-	8%	-	-
Parcel B	67%	-	33%	-	-
Parcel C	41%	-	59%	-	-

4.10. Heavy Metals Pb, Ni, Cd

In the NOM-021 are defined the normal and dangerous concentration values. For Pb and Ni in the three parcels soluble concentrations are below the normal state class, for Pb < 35 mg·Kg⁻¹, for Ni < 50 mg·Kg⁻¹.

For Cd the NOM-021 defines a normal condition if concentration is 0.35 mg·Kg⁻¹, and a dangerous concentration if it is in the range 3 - 5 mg·Kg⁻¹. Then it is allowed up to 8 times the normal concentration before it can be considered a dangerous concentration, in parcel A only 8% of the samples has 3.2 times the normal value, for parcel B 75% of the samples have concentrations being 1 - 1.4 times the normal value; and parcel C 100% of the samples are in the range of 1 - 2.7 times the normal value. Therefore none of the parcels exhibit a dangerous condition for Cd, also it is useful that pH is in the alkaline condition since this restricts metal mobility.

4.11. Pearson Correlation

This statistical analysis was applied for the three parcels, in **Figure 2**, it is shown the one for Parcel A, in **Figure 3**, the one for parcel B and in **Figure 4**, the one for parcel C. In the insert are indicated the assigned ranges with their corresponding color. Also considering that meaningful correlations correspond to the regression values above 0.4, the number of meaningful interactions is indicated in the insert. After applying the statistical analysis, it was possible to compare and find similar interaction between chemical parameters.

From the information in **Figures 2-4**, it is found that all parcels exhibit a similar positive correlation in the pairs CE-Cl, NO₂-Fe, Cr-Cu, Cr-Zn, Cu-Zn and Cd-Zn. Parcels A and B have similar correlation in the pairs CE-SO₄, SO₄-Cl, Cr-Zn. Also, for parcels B and C there is coincidence in the pairs Cr-Ni, Cr-Zn,

Table 10. Synthesis of meaningful correlations exhibit by the parcels A, B, and C.

Criteria	Parcel A	Parcel B	Parcel C	Total per row
Very strong (-)	3	0	0	3
Strong (-)	4	8	12	24
Moderate (-)	10	8	26	44
Moderate (+)	36	44	18	98
Strong (+)	15	12	18	45
Very strong (+)	5	12	15	32
Total per column	73	74	89	246

Maximum number of interactions in bold type.

Ni-Cu, Ni-Cd, Ni-Zn, Cu-Cd. Finally parcels A and C has one coincidence in the pair TH-K.

Table 10 reported a comparison of the meaningful interactions for the three parcels in the categories of very strong (-), strong (-), moderate, strong (+), very strong (+).

In this table, it can be observed that the maximum number of meaningful interaction corresponds to parcel C, and parcel A has a similar amount to parcel B. Although parcel A is the only one having a very strong (-) interactions; parcel A and B have similar number of meaningful interactions in the negative categories, but C has the maximum number of negative interactions. The maximum number of positive interactions corresponds to parcel B; also, B has the highest number of interactions in the moderate (+) category.

5. Conclusion

In general, it can be concluded that bioremediated parcel (C) has most uniform pH, negligible salinity risk estimated from EC and SAR, its SOM is in the medium content but bioremediation has enabled heavy metal accumulation at higher values in respect to A and B.

Natural attenuated parcel (A) has some spots with lower pH, exhibits a moderately saline risk from EC data, and no sodicity risk from SAR data, it has a high content of SOM and the lower content in Heavy metals.

Unaffected parcel or the clean one (B) exhibits the higher pH values, EC data indicates a slightly saline condition, SOM ranges from high to very high, and the heavy metals content is medium not reaching a dangerous level.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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