Evaluation of contaminants in agricultural soils in an Irrigation District in Colombia

Martínez-Mera Eliana Andrea a,b,*, Torregroza-Espinosa Ana Carolina a, Crissien-Borrero Tito José c, Marrugo-Negrete José Luis a,c, González-Márquez Luis Carlos e

a Universidad de la Costa CUC, Grupo de Investigaciones en Agroindustrial Sostenible, Calle 58#55-66, Barranquilla, Colombia
b Estudiante de Doctorado en Ciencias Biológicas Agropecuarias, Universidad Autónoma de Nayarit, México
c Universidad de la Costa CUC, Grupo de Investigaciones en Desarrollo Agroindustrial Sostenible, Calle 58#55-66, Barranquilla, Colombia
d Universidad de Córdoba, Grupo de Investigaciones en Aguas, Química Aplicada y Ambiental, Carrera 6 #76-103, Montería, Córdoba, Colombia
e Universidad Autónoma de Occidente, Unidad Regional Guasave, Departamento de Ingeniería y Tecnología, Avenida Universidad s/n, CP 81048, Sinaloa, Mexico

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A B S T R A C T

This study evaluated the concentration and distribution of heavy metals (HM) (Cr, Ni, Pb, Cd, Hg, and Zn) and pesticides (organochlorine and organophosphorus) and the relationship of these pollutants with the physicochemical properties of agricultural soils in an Irrigation District (ID) in Colombia. Soils samples were analyzed for pH, humidity, organic matter, P total, N total, electric conductivity (EC), cation exchange capacity, and texture (% sand, clay and silt). Canonical correlation was used to determine the relationship between soil properties and HM. Soil pollution were evaluated with geoaccumulation index (Igeo), contamination factor (CF), degree of contamination (Cdeg) and pollution load index (PLI). The results indicated that, in general, the soils had adequate physicochemical conditions for the establishment and development of crops. The presence of pesticides in the soils was not reported. However, concentrations HM was detected (Zn > Cr > Ni > Pb > Hg > Cd). The soil characteristics (silt, clay, pH and EC) contributed to explain HM concentrations. The Igeo indicated that the soils are heavily contaminated with Hg (3 < Igeo < 4). The CF was very high for Hg (>6). The Cdeg presented moderate to considerable variations (<6Cdeg<24). The PLI indicated that the soils are contaminated (1.308). The presence of HM may be associated with the agricultural and quarries activities carried out near the ID. The impact caused by high concentrations of HM can lead environmental, economic and social impacts in the study zone.

1. Introduction

Soil is the most important basic natural resource for the support of agricultural production systems (De Alba et al., 2003) and the maintenance of productivity in these ecosystems depends on their physico-chemical and biological characteristics (Garcia et al., 2012; Martínez-Mera et al., 2017). However, soil is very sensitive to environmental variations (Chen et al., 2010). The anthropogenic activities of mining, changes in the use of soils and, use of agrochemicals in conventional agriculture have altered physicochemical properties, decreased edaphic populations and increased concentrations of some pollutants (Jaurixje et al., 2013). In this sense, agricultural production systems are a source of pollutants and, according with the physicochemical characteristics of the soil, facilitate their transfer through soil-plant, soil-groundwater and surface-soil water (Kabata-Pendias, 2011).

The pollutants in agricultural soils include HM and pesticides (Marković et al., 2010). HM are naturally present in small quantities or traces in the Earth’s crust, soils and plants. Many of them are essential for the growth and development of plants, animals and humans (Galán-Huertos and Romero-Baena, 2008; Marković et al., 2010). These natural concentrations can be affected by the implementation of synthetic fertilizers and pesticides, manure and conventional solid waste compost (Wu et al., 2012; Alloway, 2013). High concentrations of HM can affect the environmental health of ecosystems, placing biota at risk (Galán-Huertos and Romero-Baena, 2008). On the other hand, pesticides are used to combat, repel and/or prevent unwanted organisms (plants or animals) during agricultural production (Gilden et al., 2010). In Colombia, the intensive use of these products has increased the degradation of agricultural soils (Silva and Correa, 2009). Chemical agriculture models that use synthetic products such as fertilizers and pesticides...
are an important source of pollutants in edaphic systems (Rueda-Saá et al., 2011; Jiao et al., 2012).

Several studies have been carried out on the evaluation of physicochemical characteristics in soils and the presence of contaminants (Silviera et al., 2003; Alloway, 2013; Simón et al., 2013). Particularly in Colombia, progress has been made mainly in the departments of Atlántico and Córdoba (Yacomelo, 2014; Roqueme et al., 2014; Marrugo-Negrete et al., 2017). The state of physicochemical properties in soils determines the quality and health of the soil because processes of adsorption, transport and degradation of contaminants depend on these characteristics (Bautista-Cruz et al., 2004). In fact, the physicochemical properties of soils, such as pH, OM, texture, mineralogy of clays, potential oxide reduction, carbonates, salinity and iron and manganese oxides and hydroxides, allow for the precipitation, dissolution and solubility of metals and pesticides (Galán-Huertos and Romero-Baena, 2008).

The use and proper management of soils is the most important method to conserve the soil environment. Otherwise, processes are generated that cause, not only loss of productive capacity, but also negative environmental, social and economic impacts (UPRA, 2013). Therefore, in the present study, the concentration of pollutants (HM and pesticides) was evaluated, as well as the relationship with physicochemical characteristics of agricultural soils in the South of the Atlántico Department. Studies are needed for a baseline for the definition of sustainable management strategies in this type of ecosystem because Colombia does not have a regulatory framework for concentrations of contaminants in soils (Rueda-Saá et al., 2011).

2. Methodology

2.1. Description of the study area

The municipality of Repelon is located to the west of the department of Atlántico (10° 29' 40" N and 75° 08' 27" W), with a surface area covers 35,172 ha (10.6% of the total area of the department of Atlántico). The Guajaro reservoir (10° 42' N and 75° 6' W) stands out, a lentic body that supply the community for drinking water and for different productive activities. In its beginnings, the reservoir was capable of storing about 400,000,000 m³ of water, in an area of 16,000 ha with five meters of average depth. Currently, El Guajaro has an extension of 11,647 ha, a perimeter of 114.28 km and an effective volume of 240,000,000 m³.
There are quarries in the middle and North area of El Guajaro, from which is extracted mainly construction material (sand, clay and limestone for cement, gravel and stone) (Carrillo and Cajuste, 1995). The most important economic activity in the region is the agriculture (CRA, 2014). An irrigation system (Fig. 1) was constructed to transport water to the crops. This ID covering an area 4,000 ha, and it is supplied by the waters from the El Guajaro reservoir through a catchment channel. The irrigation system consists of a pumping station that transports water to two channels. From there, the upper distribution channel (15 km long) and lower channel (12 km long) facilitate irrigation through gravity (CRA, 2014). In this area, the main crops are, i.e. cotton, tomato, corn, sorghum, cassava, banana, rice, guava, papaya, and mango. The agricultural activity of transitory crops intensifies during the months of August–January (Alcaldía de Repelón-Atlántico, 2016).

As for the hydrometeorological conditions of the area, the temperatures are between 28 and 32 °C. Rainfall varies according to the time of year: during the dry season (January–July), the average is 39 mm and, in the rainy season, it is 117.2 mm (August–December), with an annual average of 50 mm (Climate, 2017). However, the hydrometeorological conditions of the area result from the marked interannual variability, produced by the climatic anomalies El Niño and La Niña (Ruiz-Cabarcas and Pabón-Cuaredo, 2013).

In terms of the general characteristics of the agricultural soils in southern Atlántico, the Repelón ID is located in quaternary deposits that occupy areas with a flat relief. The western side of the southern of Atlántico department has 50% of soils formed from clay sedimentary materials that are low in evolution, superficial, well drained, low to moderate in fertility and susceptible to erosion. These soils according to the texture, are classified as sandy loam clay and sandy loam at a depth of 0–30 cm and belong to the Inceptisol order. Table 1 describes the classification of the agricultural soils of the Repelón ID, suggesting a capacity for use, productivity and physicochemical characteristics (IGAC, 2008).

### 2.2. Field phase

The field area was divided in three zones: northern zone (soil samples 1 to 4), central zone (soil samples 5 to 8) and southern zone (soil samples 9 to 10). In areas with a history of agricultural activity, during the dry season a total of 10 topsoil samples (0–30 cm depth) were collected, which were obtained after the removal of the plant material from the soil surface, each soil sample comprised a composite of three subsamples. The characteristics and the locations of the sampling sites are shown in Table 2 and Fig. 1. Samples for the physicochemical parameters and HM were stored in polyethylene bags. The samples for the pesticide analysis were wrapped in aluminum foil before being packed in polyethylene bags. All samples were transported under a controlled temperature (4 ± 1 °C) to the environmental laboratory of the Universidad de la Costa (CUC).

### 2.3. Laboratory phase

The physicochemical parameters were determined: moisture with the gravimetric method (IGAC, 2006), pH with the potentiometric method (NTC 5264, 2008), electrical conductivity (ECe, g) with a conductivity meter (model EC300), total N (N total) with the Kjeldahl method (NTC 5889, 2011), organic matter (OM) from total organic carbon (Walkley--Black method) using a conversion factor (%C * 1.74) (IGAC, 2006), and cation exchange capacity (CEC) with the saturation method with ammonium acetate (NTC 5268, 2014). Additionally, the texture parameters (Bouyoucos-Densimeter Hydrometer) and total phosphorus (P) (Olsen et al., 1954) were determined in a certified laboratory (Zonas Costeras S.A.S.).

Pesticide samples were analyzed with gas chromatography with an electron capture detector (CG-ECD), using EPA Method 8081B (US-EPA, 2007a) and 8141B (US-EPA, 2007b) for organochlorine and organophosphorus pesticides, respectively. The detection limit was 2 μg/kg for organochlorine pesticides and 5 μg/kg for organophosphorus pesticides. The quantification of HM zinc (Zn), nickel (Ni), cadmium (Cd), lead (Pb), and chromium (Cr), 0.5g of soil samples were digested with HNO3/HCl 8:2 v/v in a microwave using EPA Method 3051A (US-EPA, 2007c). Additionally, concentrations of Hg heavy metal were evaluated using EPA Method 7417B, where 0.5g of soil sample was digested whit H2SO4/HNO3 7.3v/v and 5% w/v KMnO4 at 100 °C for 1h (US-EPA, 2007d). The detection limits (mg/Kg) varied for the metals (Zn = 5.0, Cr = 3.0, Ni = 20, Pb = 0.07, Cd = 0.022 and Hg = 0.001). The pesticides and heavy metals concentrations were calculated as the mean from triplicate determinations. These analyzes were carried out in the Toxicology and Environmental Management Laboratory of the Universidad de Córdoba-Colombia.

### 2.4. Quantification of soil pollution

#### 2.4.1. Geocaccumulation index (Igeo)

The Igeo for the metals were determined using:

$$ Igeo = \log_{1.5} \left( \frac{Cn}{Bn} \right) $$

where Cn is the concentration of metal examined in soil samples and Bn is the geochemical background concentration of the metal (n). Factor 1.5 is the background matrix correction factor due to lithologic. This index ranges from <0 uncontaminated, 0 < Igeo < 1 low contamination, 1 < Igeo < 2 moderately contaminated, 2 < Igeo < 3 highly contaminated, 3 < Igeo < 4 heavily contaminated, 4 < Igeo < 5 very heavily contaminated and >6 extremely contaminated (Müller, 1981).
2.4.2. Contamination factor (CF)

The level of contamination of soil by metal is expressed in terms of a CF calculated as:

\[ CF = \frac{C_{metal}}{C_{background value}} \]

Where \( C_{metal} \) is the concentration of metal examined in soil samples and \( C_{background value} \) is the geochemical background concentration of the metal. This index ranges from \( CF < 1 \) refers to low contamination; \( 1 < CF < 3 \) means moderate contamination; \( 3 < CF < 6 \) indicates considerable contamination and \( CF > 6 \) is very high contamination. The CF is a single element index (Hakanson, 1980).

2.4.3. Contamination degree (Cdeg)

The Cdeg represents the sum of all pollution factors for all elements examined in a given site and it is determined using:

\[ C_{deg} = \sum_{i=1}^{n} CF_i \]

Where \( n \) are all the metals evaluated. There are four classes: \( C_{deg} < n \) (low degree of contamination), \( n < C_{deg} < 2n \) (moderate), \( 2n < C_{deg} < 4n \) (considerable) and \( C_{deg} > 4n \) (very high degree of contamination) (Hakanson, 1980).

2.4.4. Pollution load index (PLI)

The PLI is calculated by obtaining the n-root from the CF that were obtained for all the metals studied (n). The PLI was determined using (Tomlinson et al., 1980):

\[ PLI = \sqrt[CF]{CF1*CF2*...CFn} \]

According to the CF value, the PLI was categorized as \(<1 \) uncontaminated and \( >1 \) contaminated; with this value the relationship with soil quality was determined (Iqbal et al., 2016).

Taking in account that in Repelón Municipality (Colombia) does not have local information about values of background or natural concentration elements, the values of background were taken from the limits proposed by the NOAA, which presents screening concentrations for contamination elements (Hakanson, 1980).

2.5. Information analysis

Multivariate cluster analysis is presented in a dendrogram for metals and soils. The normality of the data was evaluated prior using Shapiro-Wilk test (Yap and Sim, 2011). As HM concentrations and soil properties did not show normal distribution, values were log-transformed. With the log-transformed data a multiple comparison was evaluated using a canonical correlation analysis, and find out the contribution of physicochemical properties of soils and heavy metals. Statistical analysis was performed with R.

3. Results

3.1. Physicochemical parameters

The physicochemical characteristics of the soil samples are shown in Table 3. The soils showed differences between the sites sampled. The pH was found to be slightly acidic (6.4) to slightly alkaline (7.2). The soil moisture was low, between 0.91-5.99%. The organic matter and total phosphorus presented values between 2.90-6.45% and 76.2–113.0 mg/kg, respectively, which were high (IGAC, 2008; Martínez et al., 2008; Novello and Quintero, 2009). The total N of the soils varied from very low (0.09%) to low (>0.15%) (Hoskins, 2017). On the other hand, the \( EC_{1.5} \) presented values < 0.35 in all of the soil samples, indicating that the soils do not have salinity problems (Andrades and Martínez, 2014). The CEC was high (25–40 meq/100g) (Castellanos, 2016). Finally, three texture groups were found: silty clay loam (14.3% sand, 45.8% silty, 49.9% clay) and clay (14% sand, 39.8% silty, 46.2% clay) in the northern zone; silty clay (9.6% sand, 44.3% silty, 46.1% clay) in the central zone; and clay (6.5% sand, 38.4% silty, 55.1% clay) in the southern zone.

3.2. Pesticides

The presence of organochlorine pesticides such as heptachlor benzene, aldrin, endosulfan, dieldrin, endrin, and 4,4′DDT and organophosphorus pesticides such as malathion, chlorpyrifos-methyl, fention, tridemofon, diazinon, cis-chlortrifenvinos and dimethoate was not reported. The results obtained were below the detection limit of the equipment (<2 µg/kg for organochlorine pesticides and <5 µg/kg for organophosphorus pesticides).

3.3. Heavy metals

The concentrations of HM showed variations in the soil samples. The average levels of HM in the agricultural soils follow a decreasing order as: \( Zn > Cr > Ni > Pb > Hg \). The HM \( Zn, Cr, Ni \) and \( Cd \) showed a similar pattern of concentrations in the field area. In general, highest concentrations (\( Zn, Cr, Ni, Hg \) and \( Cd \)) were found in the southern area except for the \( Pb \) that showed high concentration in the central zone. Additionally, northern and central zones had little differences in concentrations for \( Zn, Cr, Ni \) and \( Cd \). Similar pattern was showed for \( Pb \) in northern and southern zone. Finally, \( Hg \) showed variations between central (high concentration) and northern zone (low concentration) in comparison with southern zone.

On the other hand, the HM studied were highest than the world soil reference (NOAA) (Table 4). Concentrations of \( Hg \) were 8.5 times higher than reference, followed by \( Ni \) (3.3 times), \( Zn \) (2.01 times), \( Cr \) (1.84 times), \( Pb \) (0.34 times) and \( Cd \) (0.2 times) that was the HM in lowest concentration.

Table 3

| Soil sampling | pH    | Humidity (%) | OM (%) | P (mg/Kg) | N total (%) | EC (dS/m) | CEC (meq/100g) | Texture     |
|---------------|-------|--------------|--------|-----------|-------------|-----------|----------------|-------------|
| S1            | 7.2   | 4.25         | 2.90   | 76.2      | 0.15        | 0.10      | 35.4           | sicl        |
| S2            | 6.8   | 3.95         | 5.20   | 90.6      | 0.07        | 0.03      | 35.3           | sicl        |
| S3            | 6.9   | 5.77         | 4.05   | 94.4      | 0.11        | 0.01      | 41.4           | c           |
| S4            | 7.2   | 3.71         | 6.00   | 98.5      | 0.26        | 0.02      | 39.2           | c           |
| S5            | 7.2   | 1.48         | 5.60   | 101.6     | 0.12        | 0.07      | 39.3           | sic         |
| S6            | 7.2   | 4.81         | 5.97   | 113.0     | 0.11        | 0.02      | 48.8           | sicl        |
| S7            | 6.5   | 0.91         | 3.42   | 106.3     | 0.26        | 0.04      | 39.1           | sicl        |
| S8            | 7.2   | 5.99         | 6.45   | 108.5     | 0.30        | 0.01      | 47.2           | sic         |
| S9            | 6.4   | 2.43         | 3.83   | 102.8     | 0.23        | 0.01      | 54.4           | c           |
| S10           | 6.4   | 5.61         | 3.58   | 111.3     | 0.16        | 0.04      | 51.9           | c           |

OM (Organic Matter); P (Phosphorus); N total (total Nitrogen); EC (Electric Conductivity); CEC (Cation Exchange Capacity); Texture: sicl (silty clay loam), c (clay), sic (silty clay).
3.3.1. Geoaccumulation index (Igeo)

The concentrations of Pb and Cd did not represent contamination in the agricultural soils of the Repelón ID. The HM Zn and Cr presented a slight degree of contamination, Ni had moderate contamination and Hg had a degree of strong contamination (Fig. 2).

3.3.2. Contamination factor (CF)

The HM in the Repelón/C19 agricultural soils presented variations in the CF. Fig. 3 shows the CF for the evaluated soils. The CF was low for Cd and Pb (0.20 and 0.33, respectively); moderate for Cr and Zn (1.84 and 2.04, respectively); considerable for Ni (3.33) and very high for Hg (8.45).

3.3.3. Contamination degree (Cdeg)

The Cdeg in the northern zone varied between moderate (9.56) to considerable (18.7) where the soil sample S4 presented high contamination degree in this zone. In the central zone, the Cdeg varied between considerable (21.0) to moderate (9.72), in this zone the soil sample S6 showed highest level of Cdeg of all soils. Finally, in southern zone the Cdeg was considerable (20.7).

3.3.4. Pollution load index (PLI)

In this study, the evaluation of the overall toxicity status of all soil samples were PLI > 1, this value suggest that quality of the agricultural soil is deteriorating (Mir-Mohammad et al., 2016). The pattern of pollution in each soil sample was similar to Cdeg, where soil samples S4 and S6 showed higher values, as the same manner in southern zone.

3.3.5. Multivariate cluster analysis

Dendrogram in Fig. 4a enabled the identification of two major clusters. Cluster 1 is composed of Pb, Hg and Cd. The second cluster is composed of Cr, Ni y Zn. Similarly, sampling points were also analyzed by clustering methods and organized in the dendrogram to identify similar groups (Fig. 4b). The sampling sites could be grouped in three clusters, with the majority in cluster 1 with 7 samples, and cluster 2 with 2 samples. In addition, among all the sampling sites, 70% represent cluster 1, with a similar percentage of samples located in the north and center zone of the Repelón ID (Fig. 4).

3.3.6. Canonical correlation analysis

The correlations between physical-chemical soil characteristics (G1) and HM concentrations (G2) in the soil samples are shown in Table 5. Six canonical correlations were obtained (L1-L6), of these correlations only L1, L2 and L3 were statistically significant (P-value < 0.01). The high correlation coefficient (near 1) means a good relation between variables, if $R^2$ is more than 0.7, it can be strongly correlated. In L1, the variability (99%) was explained by silt, clay and Cd, they had the biggest positive coefficients. Additionally, Ni and Hg had a high negative standardized coefficient. In L2, the 99% of the variability was explained by silt, Hg, Zn and Cr. Whereas EC had a high negative standardized coefficient. Finally, in L3 the 95% of the variability was explained by pH, EC, Ni and Hg. Conversely, Cd, Cr and Pb had a high negative standardized coefficient.

4. Discussion

The soils of the Repelón ID presented adequate physicochemical characteristics. The pH presented values in the range of 6.5–7.5. In general, the pH of the soils was found within the range of acceptable values for the development of crops and the availability of nutrients (Andrades and Martínez, 2014). The low moisture content of the soils was related to the sampling period (dry season). Similarly, the high OM% is associated with the fallow where the vegetation cover of the soils (grass), which facilitates the accumulation of organic waste and the low precipitation prevents water erosion (Guangwei et al., 2006). The Potal content in the soil can be altered by the removal of crops (approximately 80% is absorbed by the plants), water erosion and OM mineralization (Süner et al., 2001; Novello and Quintero, 2009). However, in the

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**Table 4**

Heavy metals concentrations in agricultural soils from Repelón (Colombia).

| Soil sampling | Heavy metals (mg/Kg) |
|---------------|----------------------|
|               | Zn       | Cr       | Ni       | Pb       | Hg       | Cd       |
| S1            | 94.1     | 68.5     | 44.2     | 4.94     | 0.09     | 0.33     |
| S2            | 99.2     | 70.4     | 47.0     | 5.18     | 0.09     | 0.33     |
| S3            | 91.5     | 73.8     | 45.2     | 5.19     | 0.10     | 0.29     |
| S4            | 75.1     | 51.0     | 34.5     | 3.88     | 0.74     | 0.19     |
| S5            | 94.5     | 68.0     | 40.0     | 4.70     | 0.90     | 0.30     |
| S6            | 92.5     | 65.9     | 42.5     | 6.51     | 0.92     | 0.31     |
| S7            | 109.3    | 70.6     | 42.6     | 5.69     | 0.10     | 0.24     |
| S8            | 98.1     | 66.6     | 43.0     | 5.15     | 0.51     | 0.32     |
| S9            | 103.3    | 71.6     | 46.4     | 6.14     | 0.73     | 0.43     |
| S10           | 109.4    | 73.9     | 47.2     | 6.38     | 0.69     | 0.43     |
| Mean          | 96.7     | 68.0     | 43.3     | 5.38     | 0.49     | 0.32     |
| NOA\(^1\)     | 48       | 37       | 13       | 16       | 0.05     | 1.5      |

The bold values in the soil sampling corresponds to each soil point that was evaluated.

\(^1\) Background (mg/Kg).

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Fig. 2. Geoaccumulation index (Igeo) of the metals analyzed in the agricultural soils of the Repelón ID.

Fig. 3. Contamination Factor (CF) of heavy metals found in agricultural soils of the Repelón ID.

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Repelón soils, these factors did not influence this nutrient. Conversely, the high content of Ptotal depend to the superficial horizon, where high concentrations of this element are found because plant residues accumulate on the surface (Novello and Quintero, 2009). The low Ntotal content was related to the variability in soil temperature and moisture. High temperatures and low rainfall influence microbial degradation. Therefore, these variables affect the N supply capacity of the soil. A low content of salts can depend, to a large extent, on agricultural practices; during the dry season, the application of fertilizers is very low. Finally, the high CEC was due to the absence of salts, the texture (high clay content) and the OM present in the soil (Hoskins, 2017).

In this study, the soils were class I and II due their topography (IGAC, 2008), making them suitable for agricultural activities, and the parameters Ntotal and Ptotal did not present variation in the values previously reported (low and high, respectively). However, parameters, such as pH and salinity, varied. The factors associated with changes in pH in the soil were possibly related to the agricultural history of the soils although, currently the economic agricultural activity is subject to the rainy season. The application of chemical inputs was related to changes in the pH in the soil (Martínez-Mera et al., 2017). Additonaly, La Niña phenomenon where the soils were flooded, the soil pH increased with flooding time (Kashem and Singh, 2001). On the other hand, salinity in soils can be caused by natural or anthropic processes. In the former, the soluble salts are found in the subsoil and rock deposits. On the other way, the salinity generated by agricultural activities can be caused by inadequate irrigation methods and the handling of chemical substances (McKenzie, 2013). Taking these factors into account, the decrease in salinity in Repelón soils may be related to the decrease in agricultural activities associated with climate change (dry season) or improvement of agricultural practices over time.

Although the use of LorsbanTM 4E insecticide, glyphosate herbicide and NPK 15-15-15 (Fertilizer-Triple 15) (Martínez-Mera et al., 2017) has been reported in the Repelón ID when the agricultural activities increase during rainy season, the non-detection of organochlorine and organophosphorus pesticides could be related four reasons: i). low agricultural activity during the dry season, ii). climatic conditions of the municipality, iii). physicochemical properties of the evaluated soils, and iv). environmental regulation. In terms of climatic conditions characterized by high rainfall that in some periods have caused flooding (winter wave 2010) (Ruiz-Cabarcas and Pabón-Caicedo, 2013); long periods of drought

### Table 5

| Groups | Characteristics | Canonical correlations |
|--------|-----------------|------------------------|
|        |                 | L1  | L2  | L3  | L4  | L5  | L6  |
| G1     | pH              | 0.24| 0.15| 1.18| 0.35| -0.05| 0.18|
|        | Humidity        | -0.40| 0.48| -0.15| -0.22| 0.12| -0.66|
|        | Organic matter  | 0.55| -0.20| -0.30| -0.34| -0.17| -0.52|
|        | CEC             | 0.41| -0.92| 0.88| 1.42| -0.22| 0.98|
|        | EC              | -0.38| -0.23| 0.20| -0.83| -0.15| 0.83|
|        | Total N         | 0.16| 0.00| 0.37| -0.66| 0.39| 0.21|
|        | Total P         | 0.19| -0.05| 0.10| 0.08| 0.45| 0.82|
|        | Texture Sand    | 0.36| 0.49| 0.04| 2.27| 0.80| 1.29|
|        |                 |      |      |      |      |      |      |
|        |                 | 1.40| 0.74| 0.47| 3.92| 0.02| 3.82|
|        |                |      |      |      |      |      |      |
|        | Clay            | 1.12| 0.12| 0.36| 1.27| -0.68| 2.64|
| G2     | Zn              | -0.46| 0.68| 0.09| 0.40| -1.67| -0.81|
|        | Cr              | 0.09| 0.65| -1.69| -1.05| 1.90| -0.53|
|        | Ni              | -2.94| 0.06| 4.80| -1.38| 0.64| -0.44|
|        | Pb              | 0.59| -0.31| -1.19| 0.14| -0.28| 1.86|
|        | Hg              | -1.81| 0.97| 1.60| -0.28| 1.08| -0.53|
|        | Cd              | 3.16| -0.24| -1.86| 1.40| -0.78| 0.20|
|        |                |      |      |      |      |      |      |
|        | R²              | 0.99| 0.99| 0.95| 0.82| 0.39| 0.04|
|        | P-value         | 0.00| 0.00| 0.01| 0.22| 0.93| 0.99|

P-value<0.01 Significant correlation.
conditions and high solar radiation, during 2016 the variation of rainfall was 0.2 mm (January) and 256.11 mm (May) with temperature between 36 °C (March) and 32 °C (November) and average of ultraviolet index 7–9 (very high harmful ultraviolet radiation) (Weather Online, 2018); these conditions favor photolysis of pesticides and increased evaporation of volatile or semi-volatile substances (Narváez et al., 2012). Whereas, during periods of high rainfall, the soil becomes saturated, favoring the leaching of pesticides (Uzcátegui et al., 2011; Ruiz-Cabarcas and Pabón-Caicedo, 2013). In relation to physicochemical properties, such as high OM and clay, they have the ability to adsorb or immobilizing pesticides, leaving them unavailable for biodegradation (Cornejo and Jamet, 2000). On the other hand, the Colombian Agricultural Institute (ICA) in Resolution 2189 in 1974, prohibited the sale of fungicides that containing phenylmecury, chemical inputs were use over 50 years ago. Additionally, in Resolution 366 in 1987, and Resolutions 531, 540, 723, 724 and 874 in 1998, prohibited the sale of insecticides containing active ingredients such as aldrin, heptachlor, dieldrin, chlordane and chlormethyl; it is likely that these pesticides characterized by their persistence, have degraded during the 28 years that have clape and these regulations are being complied with (ICA, 2002). The commonly used pesticides are classified as organophosphates, with high toxicity and low chemical stability; therefore, they have high degradability (Silveira et al., 2003). Taking into account the fact that the average life span of LorscheTM 4E (30–60 days) and glyphosate (1–130 days) vary depending on the soil and climatic conditions, this condition is associated with the absence of pesticides in the analyzed soils because the highest frequency of application occurs during the rainy season.

The indicators to evaluate the contamination by HM presented variati ons, and showed that in general the ID is contaminated. Pollution sources are associated with natural phenomenon and anthropogenic activities. During 2010 the phenomenon of flooding soil for a long period could provide availability of HM due little aeration of soil, reduction conditions are favored, this condition increases the toxicity of some metals such as Mn (manganese), Cu (copper), Zn, Cd, and Cr (Poot et al., 2007; Reichaman, 2002). On the other hand, the anthropogenic activities where the municipality of Repelón is part of the Calamarí Mining District and has 27 active mining operations (where 9 are illegal), taking up approximately 50 ha in areas surrounding the El Guájar reservoir that generate problems in different bodies of water (Alcaldía de Repelón-Atlántico, 2017). In the study area, there are quarries in the middle and north area of El Guájar, from which is extracted mainly construction material (gravel, sand, stone and limestone), activity that possibly by erosive processes accumulate metals in particular areas (CRA-CRADIQUE, 2002; CRA, 2014), which could reach the El Guájar reservoir and, later, the agricultural soils of the Repelón ID through the irrigation water. Belmonte-Serrato et al. (2010) and Vallejo et al. (2016), reported that the extraction of mineral resources (represented by quarries) contributes significantly to increase the concentrations of Zn, due it contributes 10–15% of the total sediments delivered by laminar erosion, which are possibly aggregated by atmospheric deposition and runoff (CRA, 2014). This result corroborate the high concentration of Zn in comparison with the others HM. Additionally, Torregroza-Espinoza et al. (2018), reported the presence of HM (Zn, Pb, and Hg) in water and surface sediments of El Guájar Reservoir, the highest levels were found in the southwest and northern zones of this body of water, it is possible that the pollutants are associated with agricultural and mining activity, floodgate (El Guájar Reservoir with Repelón ID) and the connection with the Canal del Dique, which is part of the Magdalena river (Fig. 1). On the other hand, industrial activities (aquaculture and shrimp farm), municipal waste disposal and agricultural activities, involving irrigation and applications of chemical substances, pesticides and manure, can also be sources of HM (Belmonte-Serrato et al., 2010; Marrugo-Negrete et al., 2017). The problems associated with irrigation systems depend on the quality of the water, which can be contaminated by the main tributary or receive wastewater discharge, providing heavy metals such as Ni, Pb, Cr, Cd, Zn, Cu, Hg, Mn, and Fe (iron), among others (Kim et al., 2015). The application of fertilizers that provide macronutrients (N, P, K) contain impurities of Cd and Pb, which can significantly increase their content in the soil because of regular use since they are fundamental for the growth of the plants. Likewise, phosphate fertilizers provide Cd, Hg, Pb, Ca, Cu, As and Zn as impurities (Gimeno-García et al., 1996; Wuana and Okieimen, 2011; Alloway, 2013). Other fertilizers, such as copper sulfate and iron sulphate, contain Pb and Ni (Gimeno-García et al., 1996). Even fertilizers from animals, such as manure, can also provide As, Zn and Cu as a product of the animals’ diet (Andrades and Martínez, 2014). And some pesticides can also contribute As, Pb, Hg, Cu and Zn (Alloway, 2013; Gaw et al., 2006).

During the sampling, intensive applications of chemical products in the evaluated soils were not reported. However, historically, the municipality of Repelón is known as the agricultural pantry of the Atlántico Department. Therefore, the presence of HM in the soils cannot just be associated with mining activities; it is likely that, during the winter season when agriculture intensifies, common practices such as the application of chemical inputs are a source of HM. Mining is responsible for soil degradation. Artisanal mining processes significantly alter the landscape and cause air, soil and water pollution. Quarries are associated with forced migration and loss of soil biodiversity, and destruction of fragile ecosystems (Vallejo et al., 2016).

Dendrogram for heavy metals enabled the identification of two major clusters. Cluster 1 is composed with the heavy metals (Pb, Hg, Cd) that are related with anthropogenic activities like wastewater, waste combustion and agricultural activities (fertilization and pesticide application), specifically with the application of phosphate fertilizers (Marrugo-Negrete et al., 2017; Wuana and Okieimen, 2011). And in the Cluster 2 heavy metals (Zn, Cr, Ni) have relationship with the phenomenon of flooding soil generated by the floods of the Magdalena River or mining activities of quarries, as previously explained. In the dendrogram for sampling sites, two major clusters were observed. Cluster 2 shows the sampling site 1 to the sampling site 7, with the exception of sampling site 4, possibly grouped by agricultural activities. While the second cluster includes sites 9 and 10. These sampling sites are located in the southern zone of the ID of Repelón, and presented high values in the concentrations of all the metals evaluated. In this area, the Canal del Dique connects with El Guájar Reservoir through two floodgates (Fig. 1), where the exchange of 50,000 tons/year of sediment to the reservoir (CRA, 2014) which may explain why those soils are grouped. Similarly, that zone was the most affected by the floods caused by La Niña phenomenon.

In the present investigation, a positive correlation was observed between silt and clay with Cd, and a negative correlation between Ni and Hg, with silt and clay. In the second correlation, a positive relationship was observed between silt and Hg, Zn y Cr, and a negative relationship between CEC with Hg, Zn and Cr. In the third correlation a high negative correlation was found between the pH and the Cd, Cr and Pb concentrations, and a positive correlation between pH and Ni and Hg concentration. The soils properties play an important role reducing or increasing the availability and toxicity of metals (Galán-Huertos and Romero-Baena, 2008). In this sense, the positive correlation with silt and clay, may be explained by the presence of clay minerals and Fe and Mn oxides associated forming silt sized aggregates (Melo et al., 2000). Additionally, clay presents adsorptive properties that enhanced the retention of metals that decreases its bioavailability (Jung, 2008; Marrugo-Negrete et al., 2017). The CEC is moderately related to the content of clay and OM, thus soils retain heavy metal cations (Abumada et al., 1999; Marrugo-Negrete et al., 2017). In agreement with ICA (2008), the Caribbean soils evaluated presented high content of OM, the higher CEC has the greater the capacity of the soil to fix metals (Abumada et al., 1999). On the other hand, the negative correlation between CEC and metals concentrations, is possibly explained by the formation of chelate complexes with the OM, due the high CEC (in a function of the content of OM) influences the solubility and assimilation (Angelova et al., 2013). The adsorption and exchange of metals is generally attributed to the properties of the adsorbent, the solvent, the concentration, the valence and the degree of...
hydration of the cations (Sparks, 2003). Ions with a smaller hydration radius can get closer to the adsorption surface, and adsorption of these can be favored. The average concentration of metals in the analyzed soils was Zn > Cr > Ni > Pb > Hg > Cd; such sequence is not related to the hydration radius of the metals Pb (0.401 nm) < Ni (0.404 nm) < Cd (0.426 nm) < Zn (0.43 nm) < Cr (0.461). Finally, the pH affects several mechanisms of metal retention in soils (Carrillo and Cajuste, 1995), and can be considered the most important parameter that influences the processes of sorption-desorption, precipitation and dissolution. Likewise, the formation of complexes and the reactions of oxide-reduction where the bioavailability of the elements is inversely proportional to soil pH (Narwal et al., 1999; Bastu et al., 2005; Antoniadis et al., 2008). It is important to take in account that the bioavailability of the metal is determined by several factors including mineralogy, content of matter, capacity of cation exchange and temperature of the soil, additionally, the metal fraction and its location in the soil system (Takác et al., 2009; Nederlof et al., 1993). For this problem, there are different methods for improvement of contaminated soils like removal of contaminated soil, adding uncontaminated soil as a topdressing, use of a soil conditioner depending on the heavy metal on the soil and, improvement of water management (Swata et al., 1994).

In Latin America, Colombia is the third country with the highest water resources, climate diversity and annual precipitation rates, characteristics that favor its role in food production. Therefore, The United Nations Food and Agriculture Organization (FAO) affirms that Colombia has great potential to be a pantry of the world. However, in order to supply the world population, food production will have to be increased by 70% by the year 2050 (FAO, 2018). In this context, to ensure food supply to the world population, food production will have to be increased. The United Nations Food and Agriculture Organization (FAO) affirms that the problems with heavy metals including loss of diversity, decrease of the biological potential of the soil, zero agricultural productivity, and effects on public health as chronic-degenerative diseases in people, among others.

5. Conclusions

In the studied agricultural soils, no organochlorine or organophosphorus pesticides were detected, possibly the scarce agricultural activity at the time of sampling, the variability of the climatic conditions of the area that could favor the natural attenuation of the pesticides and the characteristics of the soils and/or compliance with agricultural regulations. In contrast, the concentration of HM in the soils varied as follows Zn > Cr > Ni > Pb > Hg > Cd. The pollution indicators showed contamination in the study area, that may be related to anthropogenic activities (quarries activities, agricultural practices and, urbanization). And the natural phenomenon such as high rainfall and flooding of soils. Likewise, the canonical analysis showed in the first correlation a positive correlation between silt and clay with Cd, and a negative correlation between Ni and Hg, with silt and clay. In the second correlation showed a positive relationship was observed between silt and Hg, Zn and Cr, and a negative relationship between CEC with Hg, Zn and Cr. In the third correlation a high negative correlation was found between the pH and the Cd, Cr and Pb concentrations. Soil properties like OM, CEC, silt and, clay contributes to HM retention by decreasing its bioavailability.

This research provides knowledge on the environmental health of the agricultural soils of the Repeñón ID. Information that can serve as a tool for defining strategies for sustainable management for the implementation of monitoring plans to quantify the vulnerability of the ecosystem and potential risk to human health being that the population depends on these natural resources for the development of their economic activities.

Declarations

Author contribution statement

Eliana Martínez, Ana Carolina Torregroza Espinosa, Tito Jose Crissien, José Marrugo-Negrete, Luis Carlos González-Márquez: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

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