# FITORREMEDIATION WITH RED MANGROVE (RHIZOPHORA MANGLE) OF COASTS CONTAMINATED WITH MERCURY, ON THE COLOMBIAN PACIFIC COAST

**BY: WILD COLOMBIA CORPORATION**

## RESUME

The biodiversity of the MPA Protected Marine Area: UTRÍA (ID 303549), on the Colombian Pacific coast, it contains high mercury concentrations from illegal gold extraction mining activities in the Atrato and Jurubid River rivers. We locate 208 sources of illegal mining in rivers surrounding the coast, which generate the felling of 16,000ha of mangroves/annuals; and the contamination of soils and wetlands with heavy metals (mercury). To extract 1gr of gold, these mining structures need four people, a backhoe to eliminate 6th ground from the forest soil; In addition, they build an artificial pool applying 1,000L of water/second and 10 g of mercury. All the residual mercury used is discharged on the MPA Urtry coast, increasing the mercury content to> 0.93 µg/g, level above international critical limits (<0.3 µg/g). The illegal miners dragan the rivers to change the course and build pools where Mercury breaks the rock that carries gold. The Colombia Wild Corporation evaluated the HG concentrations in absorbent and aerial red mangrove roots (Rhizophora Mangle)., In four coastal areas of the MPA, corresponding to the indigenous territory Emberá during the months of November 2020 (period of little rain) and January 2021 (rain period). A total of 80 roots, 10 air and 10 absorbents in each area were collected. The HG was determined by atomic absorption spectrophotometry coupled to cold hydride vapor generation and expressed in mg/kg (dry matter). The HG concentration in air and absorbent roots did not present significant differences, with values of 243.13 ± 91.14 and 300.03 ± 170.96 mg/kg, respectively. The absorbent roots presented a significantly higher HG concentration during the rainy season, with a value of 321.68 ± 85.59 mg/kg. The Emberá indigenous territory presented the highest HG value (382.46 ± 273.84 mg/kg) in the absorbent roots. These findings demonstrate that R. Mangle L. has a great capacity to incorporate HG and has mercury phytorecreader capacity in mangrove ecosystems contaminated with heavy metals.

**Keywords:** mangroves, phytoremeciation, contamination with mercury, biodiversity, Emberá indigenous community.

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## INTRODUCTION

Mangroves constitute one of the most productive ecosystems in the world and have great ecological and economic value, because they provide sites of refuge, parenting and reproduction of the diverse fauna that lives in the mangrove. In turn, the mosquito roots, the debris of the sheets of the mangrove trees, as well as the soluble organic compounds, provide nutrients and substrate for many organisms such as bivalve, crabs and several species of fish. On the other hand, mangrove ecosystems act as natural sinks, and serve as filters for sediments and nutrients, maintaining water quality. They also represent physical and biogeochemical barriers for metal pollutants and serve as flood shock absorbers (Nagelkerken et al. 2008, Zhou et al. 2011).

The mangroves have the ability to absorb heavy metals; However, high concentrations of these sediments can affect their incorporation efficiency. Additionally, the roots, leaves and fruits fall and are part of organic matter, which in turn serves as food to the bentonic community and even as a nutrient for mangroves, which leads to recirculation, bioaccumulation and biomagnification of these elements (Macfarlane et al. 2007, Wang'ondu et al. 2014).

Mercury (HG) is the element that represents the greatest concern worldwide due to its toxic action for organisms and for man. It is usually not found in the natural environment and its presence means anthropic pollution. According to the United States Environmental Protection Agency (US-PA, for its acronym in English), the HG is one of the most dangerous elements, and is even harmful to small concentrations (Posada and Arroyave 2006, ThanGaradjou et al. 2014).

Within the sources of pollution that generate HG and directly discharge their spills towards the water bodies are illegal gold extraction mining in the jungles and rivers of the Colombian Andean mountains. Once discharged in the bodies of water and deposited in the sediments, HG biotransformation begins to one of its most toxic chemical species, the methylmercury, which is then incorporated into the trophic chain (Sanders et al. 2008). This pollution causes all the discharges that are made to the bodies of water, have as a final destination the coastal areas, which has represented a health problem for marine ecosystems and biodiversity.

Canadian guidelines on sediments for the protection of aquatic life (ISQG) establish a concentration of HG not exceeding 0.17 mg/kg, while the level of probable effect (PL), parameter that Define the concentration on which adverse biological effects could occur, is greater than 0.486 mg/kg (CCME 2001): Therefore, you can have a clear idea of HG pollution problem and the damage it produces in many aquatic ecosystems .

In Colombia, there are government laws and institutions responsible for protecting mangroves. In this regard, articles 405 and 406 of the National System of Protected Areas establish that the conservation of biodiversity and the maintenance of ecological functions will be guaranteed; Also, that the State will regulate the conservation, management and sustainable use, recovery and domain limitations of fragile and threatened ecosystems (Senplades 2013).

There are currently organizations in charge of the protection of mangroves in Ecomolombia, among which are the National Coordinating Corporation for the Defense of Mangrove Ecosystem (C-Condem), which gives land to the ancestral peoples of the mangrove ecosystem and claims the right to the collective property of the Ecuadorian mangrove areas (Latorre and Farrell 2014).

The Emberá indigenous territory has extensions of land with large gold reserves, which is one of the most exploited resources in the region for more than 25 years. Mining activity is one of the main sources of pollution in the area, since for many years the effluents of such activity have been directly discharged from water courses. These are then used for irrigation, thus producing a cycle of pollution.

One of the largest mining areas in Colombia is located in the upper basin of the Atrato River, where small companies operate, most of them small, which use HG amalgation as a form of gold extraction. Approximately 1.5 t/year of HG are released to the coast of the Colombian Pacific, of which 70 % and 30 % are released with tailings (Velásquez-López et al. 2010).

Mining has caused a severe loss of biodiversity and a significant incorporation of metals, particularly HG, in the biota, not only for their discharges to the bodies of water but by the Evada concentration of atmospheric HG during burning, which can reach up to 193.8 mg/m3 (Sandoval 2001).

The objective of the present work was to determine the concentrations of HG in air and absorbent roots of Rhizophora Mangle L. located in areas of the coastal coast belonging to the indigenous territory Emberá, in the MPA: UTRÍA.

## MATERIALS AND METHODS

### Description of the study area

The investigation was carried out in the Protected Marine area, on the Colombian Pacific coast, within the indigenous territory Emberá, (303549, WDPA ID) the coastal area of the Province of Urm, located west of Colombia, which has an extension of approximately 204km2.

### Field

Sections of absorbent and aerial roots of R. mangrove were taken during November 2014 (average precipitation: 3.6 mm/m2), belonging to the time of little rain, and January 2015 (average precipitation: 37.0 mm/m2) , belonging to the rainy season. The samples were obtained using a scalpel with stainless steel leaf for each sample and subsequently placed in a hermetic closure bags previously labeled, then they moved to the laboratory in a cava with ice. A total of 80 root samples (40/era, 10/locations and 5/each type of root) were collected.

### Laboratory

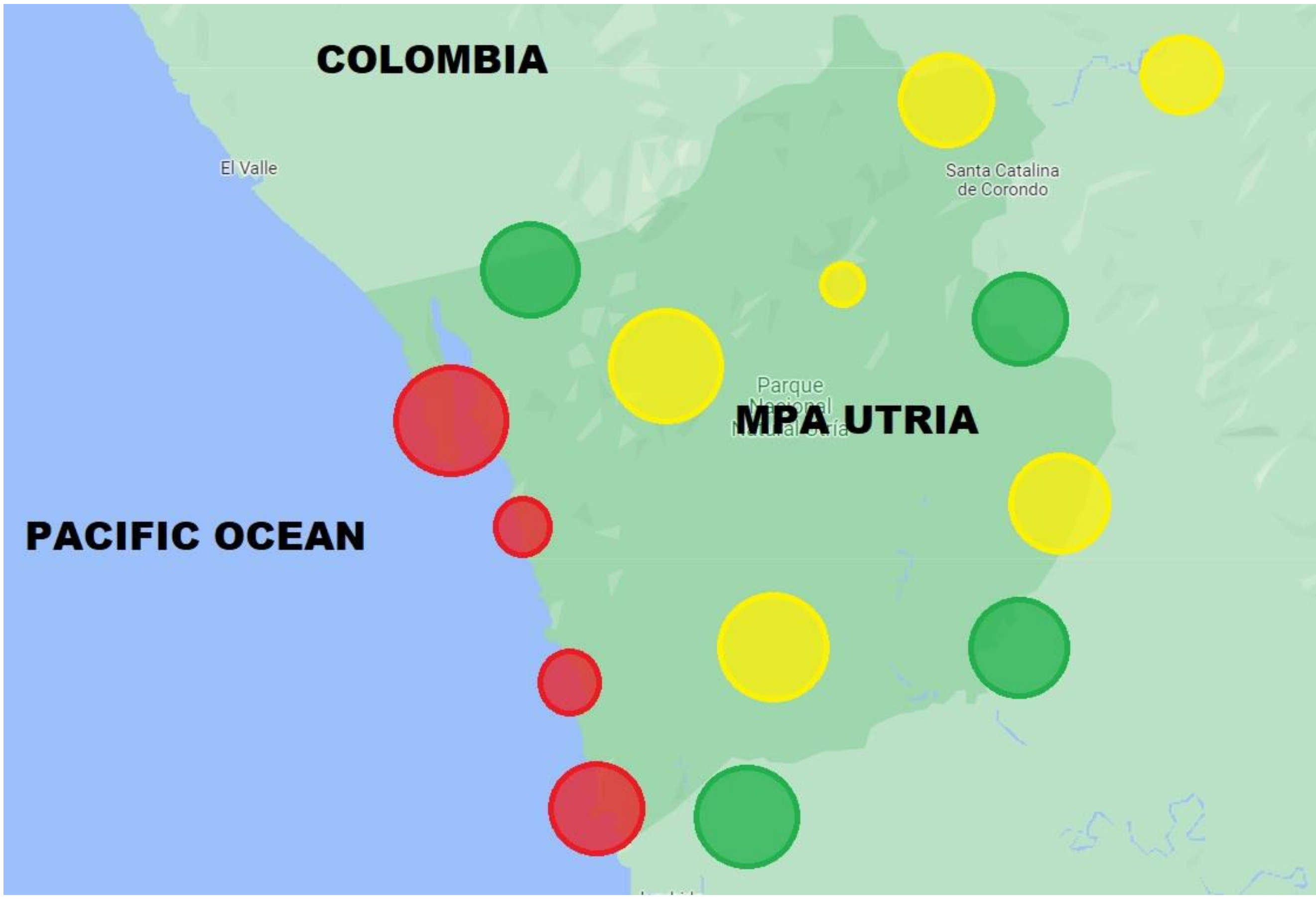
The plant material was ground to approximately 8 µm with a manual mill. Subsequently, he dried in a 60 ° C Boeco stove for 72 h. Once the sample was homogenized, a gram of them was weighed and placed in a PVC container previously washed with 10 %HNO3. The samples were predicted with 7 ml of HNO3 Concentrate Analytical grade J. T. Barker at 65 % for 24 h, then placed in a water bath for 4 h at a maximum temperature of 60 ° C until the digestion is completed. After this time, they proceeded to filter them with macherey-nagel mn615 brand filter of 125 mm and added deionized water to the sample until completing 25 ml, and then add five drops of potassium permanganate (Peven and Uhler 1993).

To determine the HG in the biological samples, a atomic absorption spectrophotometer was used to generate cold hydrors generation, using a Shimadzu AA6300 equipment. The recovery, efficiency and precision of the technique used for HG extraction was measured using the heavy certified material (IAEA-407, International Atomic Energy Agency, Monaco), for which three samples were processed in the same conditions of the curve of calibration and the samples of mangrove tissues. The theoretical concentration of HG is 0.22 with an interval of 0.216-0.228 and that obtained in this work was 0.21 ± 0.019 with an interval of 0.199-0.237 and a 97 %recovery.

### Analysis of data

Since the data did not comply with the assumptions a priori of homocedasticity and normal distribution, the non - parametric analyzes were used. To determine the differences in HG concentrations in absorbent and aerial roots of R. Mangle, the Mann-Whitney (W) test was applied, which was also made to determine the differences during the two periods of sampling. For HG levels in the four locations, a non-parametric variance analysis of Kruskal-

Wallis (KW) and the MOOD median test was applied, evaluating the significance to 5 % ($p < 0.05$). Computerized analyzes of all applied statistics were performed using the Statgraphics Centurion XVI package, v. 16.1.15.

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| | |
|---|---|
| (red) | Mangrove sampling points |
| (green) | Embera indigenous cities |
| (yellow) | Illegal mining sources with the use of mercury |

**SCALE**

1cm = 1,000meters

**Country:** COLOMBIA
**Marine protected area:** UTRIA, **ID** 303549
**City:** Chocó
**Location:** EMBERÁ INDIGENOUS TERRITORY
**Geographical coordinates:** 5°58'30.0"N 77°19'47.8"W

**Figure 1**. Project map.

## RESULTS AND DISCUSSION

The results obtained in the present investigation demonstrate a great incorporation of HG in Raíces de R. Mangle in the marine-coastal area of the URYR, Colombia, with an average HG value in the roots of 271.58 ± 131.05 mg/kg. This could be associated with the discharges of the rivers from the high basins, which have a high industrial and artisanal mining activity, the latter being the one that has probably contributed to the increase in this metal in aquatic ecosystems. Tarras-Wahlberg et al. 2001 indicated HG concentrations of 1 to 5 mg/kg in sediments of the Atrato River, estimating discharges of 289 kg/year, while Velásquez-López et al. 2010 estimated that a total HG released in that same region of 1467.05 ± 115.76 kg/year.

There are few studies that report HG concentrations in R. Mangle similar to those of this work, and those carried out have indicated lower concentrations of HG: Marchand et al. (2006) estimated an average of 0.11 mg/kg in mangroves from the coasts of the French Guiana; Qiu et al. (2011) found a concentration of 0.2 mg/kg in mangroves of Hainan Island, China, and Ding et al. (2010) detected values of 1.76 mg/kg of total HG and 0.72 mg/kg of methylmercury in mangroves of the coastal area of China (Dongzhaigang, Sanya, Shenzhen, Zhanjiang, Daguanshan and Fugong).

As far as the knowledge of the authors reaches, although literature does not show the incorporation of HG in mangrove roots with high concentrations, plants can concentrate the metal in this tissue in magnitudes far superior to those found in the environment, as is the case with The Asparagus acutifolius Esparagus, which has extremely high concentrations of HG in roots (0.6 to 443 µg/g) and stems (0.3 to 140 µg/g) when it grows in soils with a concentration of 4220 µg/g (Martínez-Coronado et Al. 2011), like this work.

The high HG levels in the coastal zone of the MPA Urry are mainly associated with the incorporation of this element in the sediments. According to studies conducted by Marín et al. (2016), HG levels in the coastal area of the MPA Utría are in a range of 3.39 to 8.86 mg/kg.

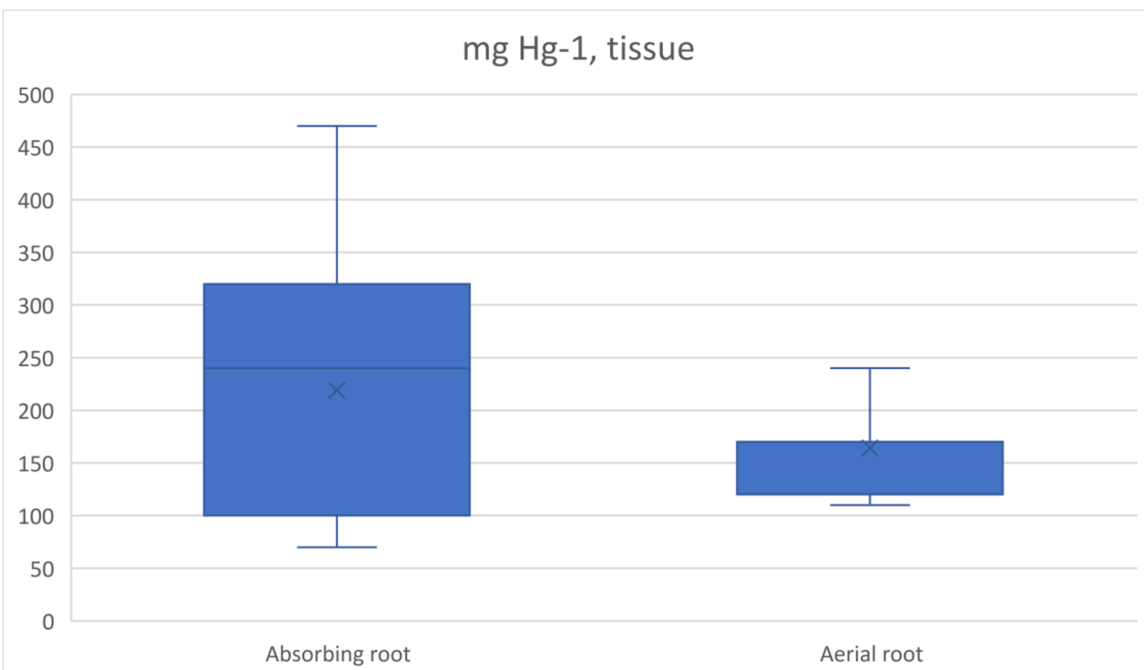
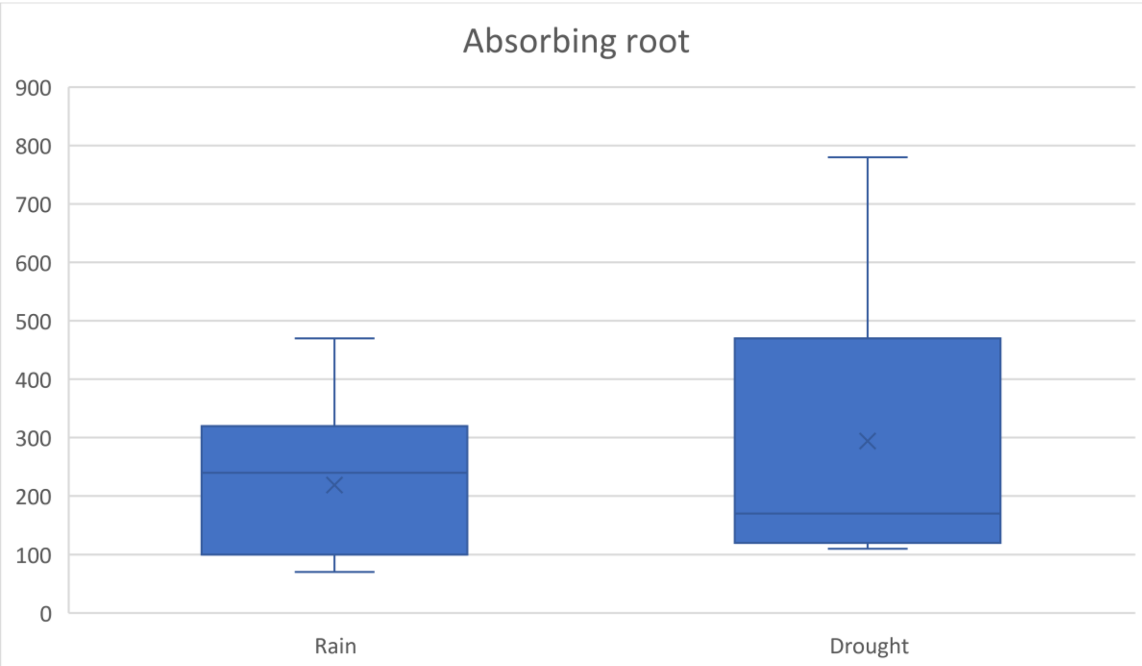



**Fig. 2** Average concentration of Hg (mg/kg in dry mass) in two types of roots of Rhizophora mangle L. in the coastal sampling area. The vertical line represents the range of values; the upper points, outliers; the mean line inside the box, the median, and the + sign, the location of the mean

The enrichment in superficial sediments is probably a consequence of industrial and domestic activities that have characterized the MPA Urtry. One of them and perhaps the most important is related to mining activities dating from 1895, approximately when the first companies dedicated to mining exploitation appeared (Murillo 2000). Another possible cause of HG enrichment in sediments is related to the use of agrochemicals (mercury oxide, mercury chloride [calomel], acetate of phenylmercury [PMA], phenylmercuric smell [PMO], Mercury alkyl, alcoxialquilo and aryry mercury) , which were prohibited since November 2005 by the US-EPA, the European Union and the Rotterdam Agreement on the prior founded consent (RAS 2011), a third source are residual discharges without prior treatment, which presumably have been made to over the years due to the urban and industrial development of Orense.




HG concentrations in aerial and absorbent roots are shown in Figure 2. On average, a concentration of 300.03 ± 170.96 mg/kg for absorbent roots was found, while in the aerial roots it was 243.13 ± 91.14 mg/kg. The Mann-Whitney test ($W = 639.0$; $p = 0.12$) did not establish statistically significant differences in HG concentrations between the two types of roots.

The compartmentalization of Hg in the different organs of the plant depends on the metal translocation mechanisms (Moreno-Jiménez et al. 2006), and in many cases it may be a strategy of the plants to accumulate more Hg in the roots than in the structures. aerial, such as leaves and fruits (Dago et al. 2014). However, the incorporation of Hg in the aerial organs depends not only on the mobilization of the metal absorbed by the roots of sediments enriched with Hg, but also on the incorporation of the Hg found in the atmosphere, since the foliar tissue is capable of to easily incorporate and release atmospheric Hg (Ericksen et al. 2003). This could occur in aerial roots, which present several pathways for Hg incorporation; In addition, its release may be associated with changes in environmental factors, particularly temperature, which establishes a more dynamic incorporation and release mechanism than absorbent roots.

The mangrove has developed throughout evolution, creating a series of mechanisms at the cellular level that allow it to establish itself in environments with high concentrations of metals. With the participation of rhizospheric microorganisms, the plants form iron plates that allow the adsorption of metals, remaining totally or partially immobilized. In absorption at the cellular level, the plant produces radical exudates, metallothioneins and phytochelatins that participate in the binding and metabolization of metals (González-Mendoza et al. 2008).

Apparently, mangroves have a high tolerance to Hg contamination, since it has been shown that red mangrove (R. mangle) seedlings treated with doses of 10 to 500 μg/g of metal in soil are not seriously affected. They are only affected when the exposure dose is higher than 500 μg/g in soil. The authors attribute the tolerance of R. mangle seedlings to high concentrations of the metal to the formation of non-toxic sulfites inside or on the root surface, to a detoxification mechanism in root tissues of ionic exclusion, or to a combination of both factors (Walsh et al. 1979).

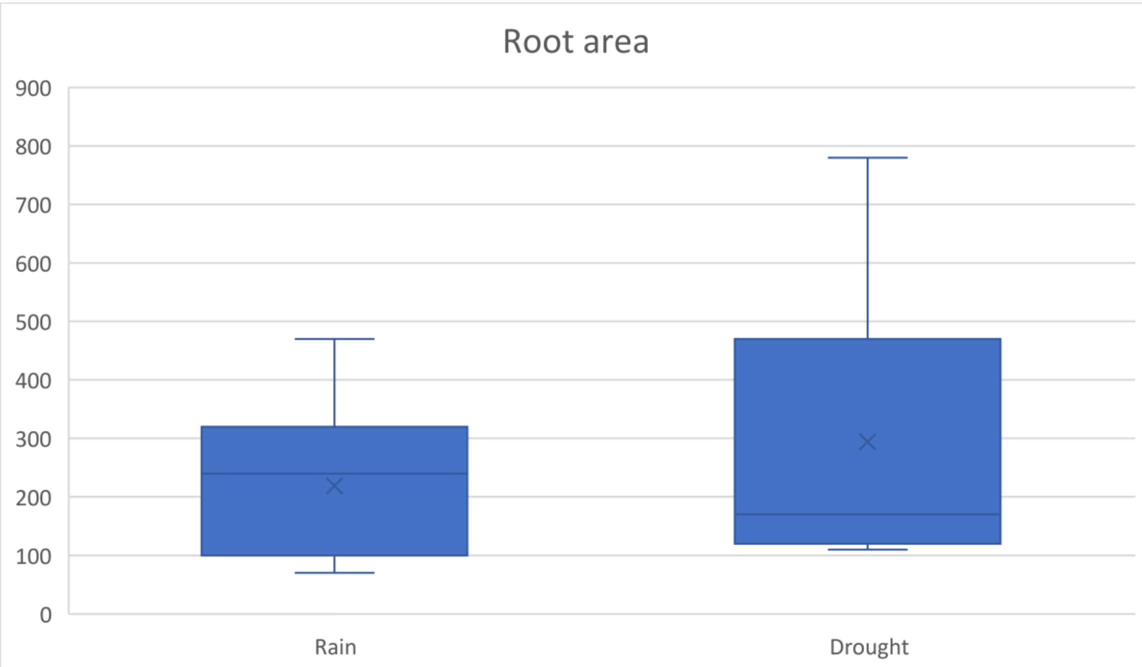



**Fig. 3** Hg concentration (mg/kg in dry mass) in absorbent and aerial roots of Rhizophora mangle L. in rainy and scarce rainy seasons in the coastal zone MPA, Utría. The vertical line represents the range of values; the upper points, outliers; the mean line inside the box, the median, and the + sign, the location of the mean

The values found in the absorbent roots and aerial roots in the rainy season were approximately 13 and 22% higher, respectively, than in the low rainy season.

The values found in the absorbent roots in the rainy season were approximately 13 % higher than in the rainy season, while in the aerial roots they were 22 % in the same season. It is possible that the greatest enrichment of sediments in coastal areas is determined by the increase in the deposition of particulate material enriched with Hg carried over during the rainy season through fluvial discharges and atmospheric precipitation.

In the study area, the rainfall begins in November and the rivers discharge their waters in the coastal areas, carrying with them the Hg from mining; there, in turn, the metal is mobilized by marine currents and deposited along coastal ecosystems (Paredes et al. 2008).

In the absorbing roots, no significant differences were obtained (KW = 1.93; p = 0.585) in relation to the locations; however, a greater concentration range is observed in Puerto Hualtaco (45.70-921.99 mg/kg) (Fig. 4). Regarding the aerial roots, there were significant differences (KW = 18.10; p = 0.0004). Mood's median test indicated that the highest Hg concentration occurred in the Estero Huaylá locality (346.48 ± 99.69 mg/kg) and the lowest in the Puerto Hualtaco locality (178.52 ± 34.53 mg/kg).

The mangrove aerial roots of Estero Huaylá presented concentrations around 34 % above the rest of the locations. The incorporation of Hg in the absorbing roots comes mainly from the bioavailable Hg in the sediment and secondly from the bioavailable in the water column (Gustin et al. 2000), this organ being a bioindicator of Hg in contaminated water bodies, while aerial roots have at least three pathways for metal uptake: 1) translocation of Hg uptake via absorbing roots (Zhang et al. 2012), 2) bioaccumulation directly from the water column at high tide, and 3) atmospheric deposition (Scholtz et al. 2003). In the case of MPA Utría, it receives water from the main mining basins of the province of Atrato international river, which divides the border between Colombia and Panamá, while the town of Estero Huaylá is characterized by being located in an estuary that is used as a discharge for wastewater from the south of the city where rivers from mining areas do not flow, so possibly atmospheric deposition and tides play an important role in the high levels of Hg that the aerial roots presented .

The recorded data indicated that the study area presents an important anthropic intervention with high Hg incorporation, which could represent a potential environmental hazard for the health of mangrove ecosystems, wildlife and the inhabitants of the MPA Utría Therefore, immediate action is required through remedial procedures.

## CONCLUSIONS

After the evaluation of the concentration of Hg in aerial and absorbing roots of mangrove (Rhizophora mangle L.), it was determined that there are high concentrations of this heavy metal in all the samples evaluated. These comprised aerial and sucker roots collected at four sampling points and two climatic seasons: dry and rainy. The highest concentration was detected in the absorbent roots in the rainy season. On the other hand, no significant differences were found in the Hg concentration at the different sampling points, although differences were found between the dry and rainy periods.

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