Spatial Analysis about Structural Patterns of Fate of Chromium (VI) in Relation to pH at Natural Sea Water Bodies

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One of the most important factors in the redox state of chromium in solution is pH, which, according to its value, can lead to oxidation of Chromium (III) to Chromium (VI). The presence of Chromium (VI) in natural waters is related to discharges from anthropogenic activities, such as leather industry, electroplating, paints, among others. The Chromium (VI) the most important toxicologically, the present state chromates, dichromates and chromic acid . The International Agency for Research on Cancer (IARC) has classified Chromium (VI) in group 1 (carcinogenic to humans) and metallic Chromium and Chromium (III) in Group 3 (not classifiable as to its human carcinogenicity. In Colombia, the permissible exposure values reported by the District Department of Health of Bogota for the general population are up to 10 $\mu g L^{-1}$and population exposed up to 20 $\mu g L^{-1}$ and the Colombian Technical Standard (NTC 813) indicates as maximum in drinking water, a concentration of 50 $\mu g L^{-1}$. In order to study the behavior of Chromium (VI) and pH in solution in marine ecosystems it was carried out systematic type sampling in a square mesh for data variables involved in the *Ciénaga de las Quintas* magrove swamp, which belongs to the internal waters system of Cartagena de Indias' Bay, Colombia. 35 field samples were taken in amber glass bottles, adjusting the pH with nitric acid, for further analysis by the Cr method 3500 B.

For the pH parameter values were taken in field with a portable pH meter. The exploratory analysis showed that the concentration data for Chromium (VI) did not conform to normal, so underwent a transformation to work with the LOG base 10, for adjustment to normal (S.W., *p>0.05*), with an average value of 3.23 $\mu g L^{-1}$. In contrast, the pH has a homogenous distribution behavior (C.V. = 1.52%) with a mean value of 8.16 $\mu g L^{-1}$; making it representative for the system. The pH values are adjusted to normal without needing any adjustment needed (S.W.; *p>0.05*). To make the structural analysis, with the aim of demonstrating spatial autocorrelation of variables, the Index of Moran (Moran, 1950) was used, which varies between 1 and -1. The pH showed slight spatial relationship or a structure related to a concentration gradient. On the other hand, the concentration of Chromium (VI) showed spatial autocorrelation, the most likely structure is the gradient type.

1. Introduction

Chromium (Cr) is a heavy metal that exists in various forms of oxidation from I to VI. Oxidation form III is not very mobile in soils and is almost insoluble in water. The trivalent form of Chromium is an essential nutrient that helps the human body to use sugar, proteins and fat. The second form of oxidation Cr (VI) is more stable, and is rarely found naturally in the environment. Its presence in the environment is mainly due to human activities (Kimbrough *et al.*, 1999). Its oxidation state is strongly dependent on factors such as the pH of the medium, temperature and light intensity, among others. Chromium is not destroyed by biological degradation, accumulating over time, causing soil and water pollution (Madhavi *et al.*, 2013). The uncontrolled dumping of Chromium into the environment is mainly due to the fact that most wastewater collection systems do not allow

the separation of urban and industrial effluents, so that wastewater from urban areas with industrial sectors is always mixed or combined. Chromium (VI) compounds are stable under aerobic conditions, but are reduced to Cr(III) compounds under anaerobic conditions. The reverse process is another possibility in an oxidizing environment. Chromium is largely bound to floating particles in water (Mwinyihija, 2010).

To characterize the origin and destination of this type of pollutants, it is not enough to make a independent statistical sampling and try to extrapolate the conditions from a point to a specific area. In this research, the behavior of Cr(VI) and pH in a sea water body, called *Ciénaga de las Quintas* mangrove swamp (Fig. 1), located in the city of *Cartagena de Indias,* Colombia, on the north coast of South America. Geostatistical techniques exploit the spatial dependence of the data (Legendre & Legendre, 1998), unlike the classical techniques of statistical analysis, that require the independence of the samples taken, regardless of their location.

This article is divided as follows: it first describes the problem and the working environment, then the statistical design technique for the collection of samples, and finally the techniques for the determination of Cr(VI) in seawater. The treatment of the data is divided into three parts: Exploratory Analysis, Structural Analysis and Predictions, both pH and Cr (VI) in the surface waters of the *Ciénaga de las Quintas* mangrove swamp, in Cartagena de Indias, Colombia. It is very important the relationship between the position and the value of the variable studied, since it was possible to predict sites where pollutants are being discharged to water bodies and there are significant changes of pH in those sites (Dermatas *et al.*, 2012).

2. Problem Description

The growth of urban centers and the use of metals such as Chromium for applications such as galvanizing, skin treatment, protection of metals and steels, causes spills, because in Colombia, very few companies make appropiate treatment to their wastes contaminated with heavy metals. The working area for this research is called *Ciénaga de las Quintas* mangrove swamp, located in the identified geographical position with the coordinates 10 ° 24'30.6 "N 75 ° 31'28.6" W, (Fig. 1) over the Caribbean region of South America, in the city of Cartagena de Indias. The *Ciénaga* borders the Bazurto grocery market, China Town neighborhood and *Sociedad Portuaria* port facilities. This swamp belongs to the internal system of streams and water bodies in the city. It is characterized by having widths between 288 and 477 m, depth of 2.25 m and an area of water surface of about 30 hectares, and the total area, including mangrove system, totalling approximately 42 hectares.

Characterizing the behavior of the contaminant Chromium (VI) and the pH of the waters of the *Ciénaga de las Quintas* from the geostatistical point of view, will give much more information, which will be useful for the implementation of decontamination technologies because it will identify critical sites of waste discharge and give insights about pH influences of the oxidation-reduction reactions of Chromium in its different states of oxidation.
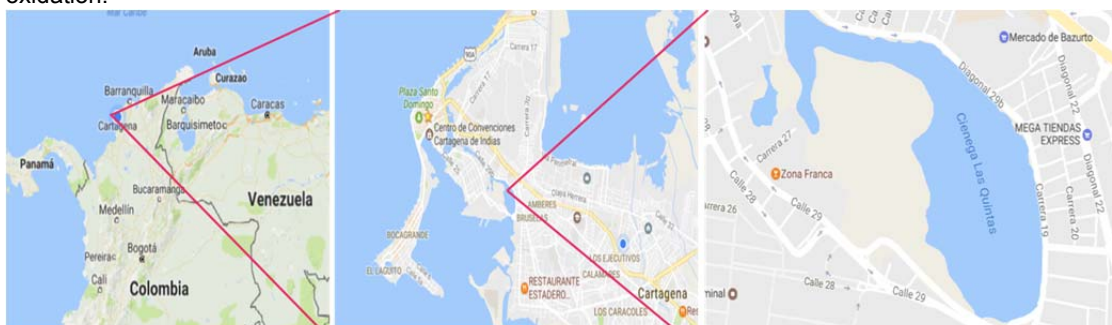

Figure 1: Geographic location of the research area, known as the Ciénaga de las Quintas mangrove swamp at the city of Cartagena de Indias, Colombia.

3. Methodology

3.1 Sampling Strategy Design

Spatial autocorrelation is a measure of the degree of similarity for a quantitative or categorical variable $Z(i, j)$ between neighboring points in space (i.e. i, j). The spatial self-correlation of one or several variables distributed in space can be described by structure functions, such as correlograms and semi-variograms (Legendre & Legendre, 1998).

For this investigation a sampling scheme was planned, with the intention of minimizing the errors for a given sample size or a minimum sampling effort for a given certainty. To meet these two approaches, that is, effort and certainty, two metodologies were taken into account: one based on a classical approach, which ignores spatial dependence between observations and can use a random scheme; and a geostatistical approach, which exploits spatial dependence and uses systematic sampling (Giraldo, 2002).

Few authors have statistically quantified the relationship between sample size or distance between samples, the spatial distribution of variables such as those discussed in this study, such as the concentration of Chromium VI in surface waters of *Ciénaga de las Quintas* and the pH of the medium and the error associated with the estimation of the mean.

With geostatistical techniques, the sampling was not based on the dispersion of the variance of the whole sample, but on seeing the variance as a function of the separation distance and direction of the samples (Hedger *et al.*, 2001). The key concept is autocorrelation: values that are in a close position between them, are more likely or likely to be similar (and thus have less variance) than others that are far away. The strength of geostatistics applications focuses on situations related to environmental variables, or any variables that can be considered regionalized (Legendre & Fortin, 1989).

The method for performing sampling is defined as random systematic, where the working area is divided into a square mesh, where each cell is the same size. To order the samples, one is defined at random and then the next one is chosen at the same distance until the mesh is finished (Fig. 2). For this case, the sample unit has 100 m of side and is square. The total work area is 411,223 m^2, approximately 42 ha (1 hectare = 10,000 m^2). and each data represents the property within the cell in the entire grid.

For this research work, the methodology was divided into three stages:

Exploratory analysis of the data: in this phase the sample data are studied without taking into account their geographical distribution. It is a stage of application of statistics. The consistency of the data is checked, eliminating those that are erroneous, and identifying the distributions from which they come.

Structural analysis: the spatial continuity of the variable is studied. At this stage the experimental variogram or any other function that explains the spatial variability is calculated, a theoretical variogram is fitted to the data and the adjustment is analyzed and interpreted to the selected parametric model.

Predictions: estimates of the variable studied in non-sampling points, considering the spatial correlation structure selected and integrating the information obtained directly in the sampling points, as well as indirectly obtained in the form of known or observed trends. Simulations can also be performed, taking into account the spatial continuity patterns chosen.

3.2 Quantification method of pH and Cr (VI) in seawater

Samples were taken in each of the cells previously identified with latitude-longitude coordinates in amber glass flasks and the pH of these was adjusted to 2 with nitric acid. Cr (VI) was quantified using the colorimetric method Cr 3500-B (APHA-AWWA-WEF., 2012). The pH of the water was measured directly into the field, using a portable pH meter OHAUS Starter ST300 model.
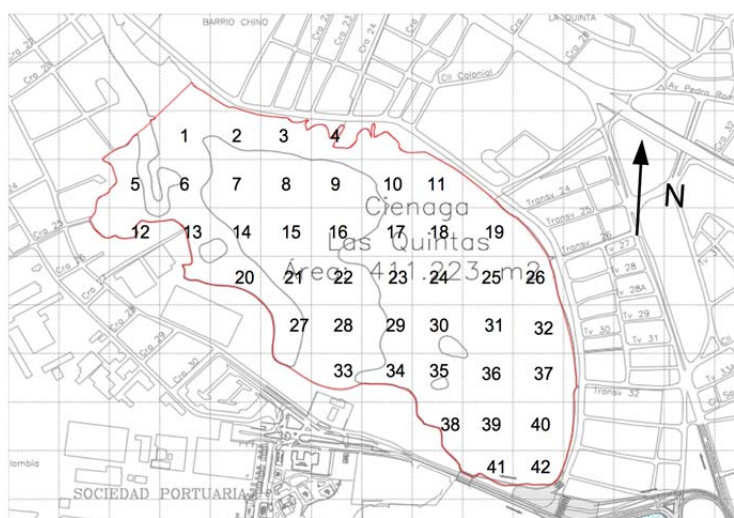

Figure 2: Square cell mesh designed for random systematic sampling, in the centre of which seawater samples were taken to quantify pH and Cr (VI).

4. Results

4.1 Exploratory Analysis

The samples were collected on August 20th, 2016, to verify the presence of Cr (VI) in the waters of *Ciénaga de las Quintas*, in addition, pH values were obtained for each point marked in Fig. 2. The univariate statistic is shown in Table 1. The sampling mesh contains 42 points, from which only 35 could be measured, since the others were in places of difficult access in the mangrove. The range of pH values ranged from 7.82 to 8.38 and the mean value was 8.1. Overall, the pH values were normally distributed, (S.W. = 0.9519, *p*-value = 0.129) although, the skewness distribution is negative (-0,77), indicating a distribution that is only slightly asymmetric, that is, that the average pH value is representative of the entire distribution and is likely to have spatial autocorrelation, but this was later verified with the Moran test. On the other hand, the concentration values of Cr (VI) are in a range from 1 to 12.2 $\mu g L^{-1}$, the concentration data of Chromium (VI) did not fit normal distribution, underwent a transformation to work with LOG base 10, for adjustment to normal (S.W., p> 0.05), with an average value of 3.23 $\mu g L^{-1}$. After the transformation of Cr (VI) concentration using LOG base 10, the distribution fitted to normal (S.W. = 0.97, *p*-value = 0.55).

Table 1: Summary of Univariate Statistics and Shapiro-Wilk (S.W.) test.

Estimator	pH	Cr(VI)	LOG$_{10}$ Cr(VI)
N	35	35	35
Min	7.8	1.0	0
Max	8.3	12.2	1.0
Mean	8.1	3.2	0.45
Variance	0.015	4.1	0.04
Skewness	-0.77	2.7	0.52
C.V.	1.5	63	48.7
S.W.	0.95	0.74	0.97
p-value	0.12	2.1E-6	0.55

4.2 Structural analysis

To verify the existence of spatial autocorrelation about the pH and Cr (VI) concentration data, the Moran Index was used (Fig. 3). The interpretation of this test is made within the content of a hypothesis contrast, where the null hypothesis (H$_0$) corresponds to a random behavior of the data, without any spatial pattern. In Figure 3a, corresponding to the behavior of pH values, little spatial autocorrelation is noticed, since no value is above the critical *p*-value (red line), that is, that the null hypothesis can not be rejected. We see a similar behavior in Figure 3b, but taking into account the variable that is being studied, it may be due to the dynamics of the water system and rainy seasons, since other studies (data not shown) demonstrate the autocorrelation In the form of gradients for Cr (VI) concentration. This type of contaminant comes from discharges of untreated sewage, which reaches these seawater bodies in a punctual way, not with regularity in time.
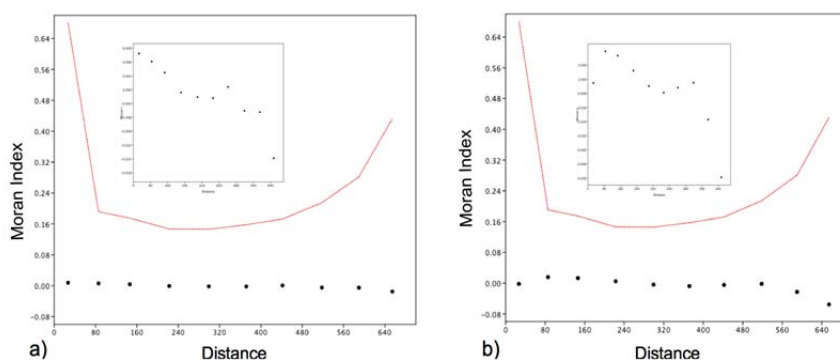

Figure 3: a) Spatial autocorrelation analysis of the pH data. b) LOG$_{10}$ Cr(VI) concentration in the work area using the Moran index.

4.3 Spatial predictions

Using information from the values obtained by the experimental work (pH and concentration of Cr (VI)) and the positions at which samples were taken, predictions of these variables were estimated. The method used was Inverse distance weighting, which is based on making predictions in non-sampled places as a linear combination of the values of sampled sites whose statistical weights are proportional to the inverse of the square of the distance. The mesh for our estimates was 100 X 100 (10,000 points); for each new point, the 10 closest neighbors were used to calculations (Fig. 4). The calculations were implemented using the software PAST v3.13 (Hammer *et al.*, 2001).
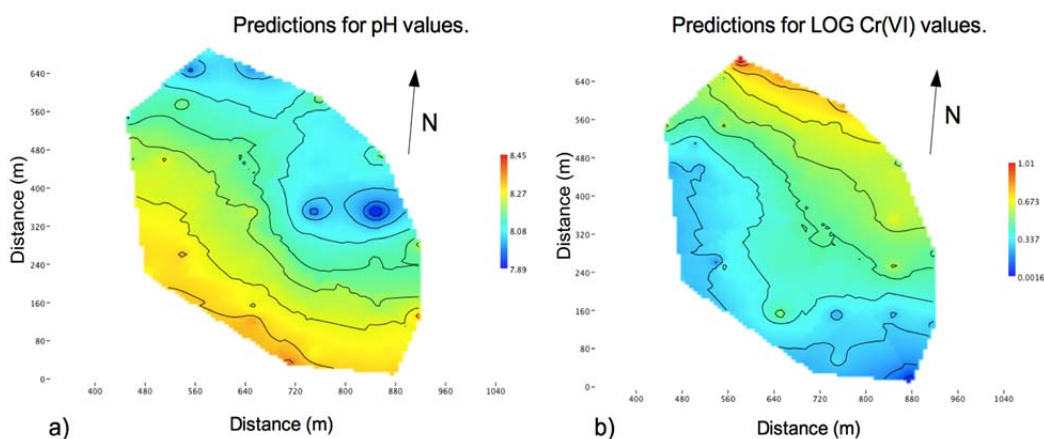

Figure 4: a) Geostatistical predictions of the pH, obtained from the points taken in the field, where the gradients in different colors are observed; b) predictions for LOG Cr(VI).

5. Conclusions

The presence of Cr (VI) in the waters of *Ciénaga de las Quintas* mangrove swamp, in Cartagena de Indias, Colombia, is evidenced. The spatial correlation of the values of Chromium (VI) concentration and the pH of the water show a relationship with the geographical position. The highest values of Cr (VI) are close to the sources of anthropogenic activity (Bazurto public market) in the north-eastern part of the mangrove swamp, as well as the lower pH values are at the sites where Cr (VI) concentration is higher, this may be due to the fact that these pH levels promote Cr (III) oxidation reactions to Cr (VI).

Cr (III) is not very soluble in water (Schroeder and Lee, 1975), unlike Cr (VI). Punctual sites where the highest concentrations of Cr (VI) are found coincide with sewage discharge sites from drainage and sewage system drainage systems, possibly bringing heavy metal residues from galvanizing workshops that do not perform wastewater treatment. The average value of the pH in the system is representative of the distribution, since its Coefficient of Variation (C.V.) is only 1.5%; despite having a gradient structure. This becomes more evident in the values of the LOG Cr (VI), with a value C.V. of 48.7%, the high values of this coefficient conceal a variability of the distribution, that in certain cases of due to concentration gradients. In the spatial predictions it is evident how the Chromium is diluted in the waters of the mangrove, since it mixes with the waters of the bay of Cartagena de Indias, in direct contact with the Caribbean Sea (Cartagena Bay).

Acknowledgments

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