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RESEARCH ARTICLE

Spatial distribution of copper and pH in soils affected by intensive industrial activities in Puchuncaví and Quintero, central Chile

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Abstract

The soils of Puchuncaví and Quintero, in the coastal area of central Chile, have been exposed to atmospheric deposition of sulfur dioxide (SO_2) and metal-rich particles from the Ventanas Industrial Complex. The objective of this study was to determine, using geostatistical tools, the spatial distribution of copper and pH in these soils. Using Universal Kriging tool for geostatistical interpolation, we generated maps of continuous distribution of Cu and pH in the soils. The distribution of these variables was related to the distance from the industrial complex and to the direction of the winds. The concentrations of Cu and acidity were higher in the surroundings to the industrial complex and in the direction of the dominant winds. Although the distributions of both variables were similar, there was no correlation between the distribution of Cu and pH, which could be due to the distinct aerial dispersion dynamics of the compounds, which causes a divergence in their deposition on the soil. Specifically, this could be due to the fact that SO_2 is smaller than the particulate matter that contains copper, so that it is capable of being dispersed over greater distances without being deposited on the soil.

Keywords: Ventanas smelter, mining, geostatistics, Cu, metal, soil acidity.

1. Introduction

The Ventanas Industrial Complex is situated on the coast of central Chile since 1964. This industrial complex originally consisted of the Ventanas Smelter and Gener Thermoelectric. Currently, there are 16 companies located in the sector. From its inauguration in the early 1960's, the industrial plants have emitted high amounts of sulfur dioxide, copper and other metals, without any measure for mitigating these emissions (Folchi, 2006). Sulfur dioxide, as well as particulate matter, have been dispersed by the wind and deposited on the soils surrounding the point of emission (Delgado and Serey, 2002). As a result, these soils have become acidified and their metal content has gradually increased, generating a loss of biodiversity, severe erosion processes and loss of agricultural productivity (De Gregori *et al*., 2003; Folchi, 2006; Ginocchio, 2000; Ginocchio *et al*., 2013; Malman *et al*., 1995).

With the entry into force of environmental regulations in 1991, these companies began to introduce corrective actions to reduce their emissions, through implementation of the "Plan for Decontamination of the Ventanas Industrial Complex" in parallel with the installation of an air quality monitoring network. Thus, since 1999, the Industrial Complex has complied with the regulation of particulate matter and SO_2 emissions (based on annual emissions) and, since 2003, has complied with the primary regulation of air quality (SAG and MINSAL, 2010).

Despite the current reduction of emissions, the cumulative environmental effects of emissions are still latent in the surrounding soils, which have become the subject of studies that seek to characterize degraded ecosystems and search for restoration options (De Gregori *et al*., 2003; Ginocchio, 2000; Ginocchio *et al*., 2013; González and Ite, 1992). These studies have been based principally on pH and metal concentrations values. Studies done on soils near the Ventanas Industrial Complex have shown that copper contamination is concentrated within the first soil layer/horizon, given that copper shows low mobility in these soils (Ginocchio *et al*., 2004; Neaman *et al*., 2009; Ulriksen *et al*., 2012). Ginocchio (2000) collecting samples from a transect found that pH varied from 4.4 to 4.8, and total copper concentrations varied between 90 to 330 mg kg^{-1} in the topsoil. De Gregori *et al*. (2003) taking samples from the principal localities near the Ventanas smelter found that total copper concentrations ranged between 250 and 530 mg kg^{-1}. The soil contamination study that had the greatest territorial coverage was that done by the Environmental Consultancy (1996). The scientists who worked on this project developed maps of the soil pH and metal concentrations, both total and bioavailable (EDTA extraction), in an area of 10 km x 9 km East of the Industrial Complex; sampling was done using a grid of 1 km x 1 km, and taking a total of 110 soil samples. The total copper concentrations were within the range of 21-850 mg kg^{-1}, while the pH was in the range of 3.6-6.8. This study identified areas where the metal concentrations and pH were above the values considered normal by these authors (Cu above 53 mg kg^{-1} and pH below 5.5). Despite identifying areas that were not affected by pollution, the results from the Environmental Consultancy's study clearly indicated that the contaminated zone extended beyond the area considered within their sampling range.

In all of the previously mentioned studies, increasing copper concentrations and acidity have been detected near the Ventanas Industrial Complex. However, none of the studies have considered an area—that corresponds to a clear territorial unit or geographical zone—great enough to allow an analysis of the true extent of the area affected by the pollution emitted by this Industrial Complex.

Methodologically, among the studies that have taken place in this area, the majority did not do any treatment of the geodata, showing only the Cu concentrations and pH found at the sampling points (De Gregori *et al*., 2003; González and Ite, 1992b). Some studies made use of mathematical interpolation in order to determine isolines with the concentrations of copper and/or pH, calculating the intermediate values using standard formulas (Environmental Consultancy, 1996; González and Berqvist, 1986). These tools are quite simple, not very exact and also assume the independence of the point values. Consequently, the objectives of this study are (1) to determine, using geostatistical tools, the spatial distribution of copper and pH in the townships of Puchuncaví and Quintero, and (2) to evaluate the factors that determine the spatial distribution of copper and pH in the studied soils.

2. Methodology

2.1. Area of study

The area of this study included the townships of Puchuncaví and Quintero (Figure 1), with a total surface area of 44,790 hectares in an irregular form, of about 20 km in width and 33 km in length. The Ventanas Industrial Complex is located at the border between the two townships. In addition, control samples were taken from the townships of Zapallar, Nogales, La Cruz, Quillota, Limache and Concón.

2.2. Selection of sampling grid

In this case, sampling was focused on existing access points, that is, the accessible areas along public roads. From 3 km to the north of the Ventanas Industrial Complex, it is possible to establish a Cartesian plane with axes that coincide with the major highways that traverse both townships: Route F-30-E which crosses both townships along the north-south axis, and Route F-20 which crosses Puchuncaví along the east-west axis (Figure 1). This division allows access for sampling in the four cardinal directions from the point of origin. In addition, alternative transects can be formed using Route F-120 and the Route F-216, allowing access to the sector to the southwest of the Industrial Complex.

Consequently, transects were formed by the 4 highways: F-30-E, F-20, F-216, and F-120, where samples were collected at a distance of approximately every 2 km. This equidistance of sampling locations allowed for the sampling to remain systematic.

Sampling was done only on soils that did not show signs of having been disturbed anthropogenically. If these conditions were not present at a predefined sampling point, sampling locations were sought that complied with these conditions within a distance of less than 2 km. Sampling was done at points that were at least 20 m from the highways in order to avoid the influence of both vehicular and foot traffic, as well as the asphalt (which is acidic), on the soil characteristics.

2.3. Soil sampling and analysis

Samples of approximately 500 g of topsoil (0-15 cm) each were collected from 177 points (Figure 1). Soil samples were dried in an oven at 40 ºC for 48 hours and then passed through a 2 mm sieve. The pH was determined in the saturated paste extract, following the method of Sadsawka *et al*. (2006). The total concentrations of Cu were determined by atomic absorption spectrophotometry (AAS; GBC, model 902, Dandenong, Victoria, Australia) after acid digestion with nitric and perchloric acid (Verlinden, 1982). Quality assurance was assessed by similarly processing (in duplicate) a certified reference soil sample (GRX-2) obtained from the United States Geological Survey.

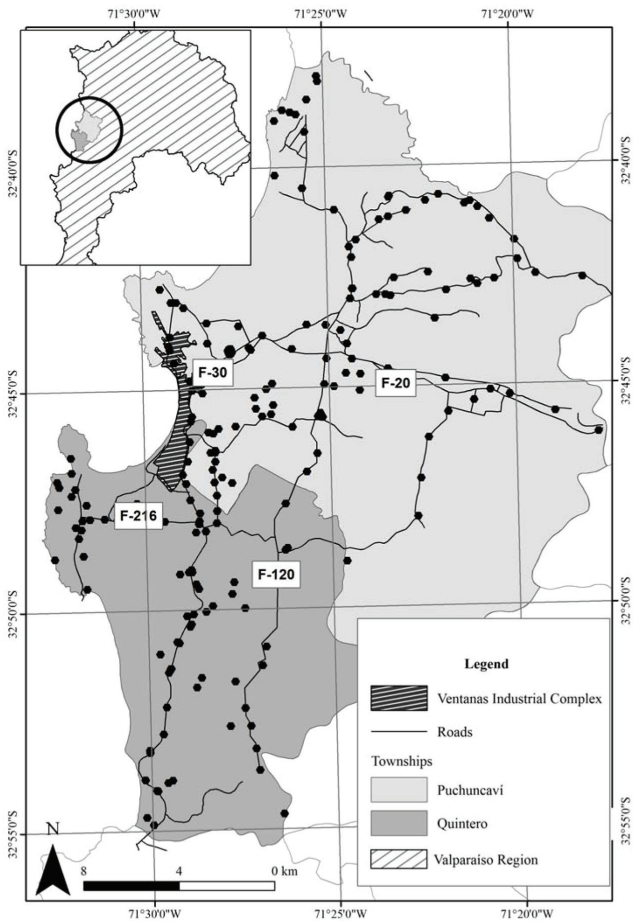

Figure 1. Location of the area of study and of the sampling points. Cartesian axes was established for sampling soils along the main highways that traverse the area of study in the North-South and East-West directions.

2.4. Method of geostatistical interpolation

The ArcGIS software program was used to manage the territorial data. Once the layer of sampled points was created, it was complemented with a layer of information of the township limits available from public databases (Biblioteca del Congreso Nacional de Chile, 2011) (Figure 1).

Geostatistical tools contained in the ArcGIS program were used for the analysis and interpolation of the spatial information. Specifically, the geostatistical tool called Kriging, using the procedure called Universal Kriging (ESRI Inc., 2003). This method considers both the distribution of the data as well as spatial trends in the data in any direction, which can then be validated (FAO, 2003). In this case, the trend can be given by the prevailing East and West winds (analysis of meteorological data provided by CODELCO-Ventanas for the year 2007-2008). Once the data were analyzed and the information was incorporated into a geostatistic model, it was then possible to do the interpolation.

2.5. Distribution of the total Cu and pH of the soil

The distribution of the continuous values of pH and Cu was done using the “Natural Breaks” method, which is included in the ArcGIS software. Four classes were established for the total copper and pH to permit visualization of the wide variation in the values of the variables. The concentration of Cu and pH values were related to the distance from the Industrial Complex using a linear regression.

2.6. Analysis of the effect of the lithology on soil pH

To correctly determine whether the acidification is of natural or an industrial origin, the natural distribution of acidity among these soils must first be estimated. The lithological units existing in the area of the study were mapped in order to analyze the effect of the lithology on the pH measured in the soils of this study. The lithological units were ranked according to their potential effect on the acidity of the soil. Specifically, soils developed on sand were expected to have lower pH, whereas soil developed on andesite, basalt, and/or limestone were expected to exhibit higher pH. Medium pH values were expected for soils developed on alluvial, fluvial and colluvial sedimentary sequences, alluvial, fluvial and colluvial deposits, quartz diorites and hornblende-biotite granodiorites. The pH values obtained were then superimposed on the lithological units in order to establish, based on a visual analysis, whether there was a correlation between the lithological units and acidity.

3. Results

3.1. Distribution of Cu in the area of study

The total Cu in the area ranged between 14 to 5,267 mg kg^{-1}, with a mean of 503 ± 506 mg kg^{-1}. However, only 3 points of the 177 sampled were greater than 2,000 mg kg^{-1}, thus they were considered outliers corresponding to specific points of pollution, as for example, soils that were very near the slag produced by the smelter. Consequently, these points were eliminated from the database. The average Cu concentration of the control soil samples taken from points outside the area of the study was 58 ± 26 mg kg^{-1} (range of 16-115 mg kg^{-1}). No significant differences were found between the means of the controls and the samples from the study area due to the wide standard deviation in the concentrations of Cu in the study area.

The distribution of the Cu concentrations in the topsoils shows a trend towards greater concentrations along the east-west axis in comparison with the north-south axis (Figure 2). This distribution coincides with the prevailing wind directions (21% prevailing to the east by day, 31% prevailing to the west by night), which was to be expected given the wide littoral plain that characterizes the area of study (Biblioteca del Congreso Nacional de Chile, 2012).

On the other hand, there is a weak correlation between the distance from the Industrial Complex and the Cu concentration of the topsoil, following the trend y=1/x (R^2=0.46 and p<0.05). The closer to the Industrial Complex, the greater were the concentrations of copper found in the soil. The inverse relationship between the Cu in the soil and the distance from the Industrial Complex has been previously reported by De Gregori *et al.* (2003), who established this relationship based on only 5 sampling points. This relationship is a clear indicator of the existence of an external source of contamination. Considering the average Cu value of the control sampling points of 59 mg kg^{-1}, and by establishing an isoline of concentration on the map, 98% of the area studied would exceed this value.

3.2. Distribution of pH in the area of study

The topsoil pH in the area of study ranged from 4.4 to 8.2, with a mean of 6.4 ± 3.2, while the pH of the control sample points averaged 7.1 ± 0.6. There was no significant difference between the means of the control samples and those of the area of study due to the wide standard deviation in pH values in the study area.

The four pH ranges offered by the ArcGIS software could be labeled "very acid" (4.4-5.9), "acid" (6-6.3), "slightly acid" (6.4-6.7) and "neutral-alkaline" (6.8-8.3). Under this denomination, 10% of the surface area was "very acid", 37% was categorized as "acid" and 53% was categorized as "neutral-alkaline".

The distribution of pH in the area of the study (Figure 3) demonstrated that, in the immediate surroundings of the Industrial Complex, the pH values tend towards neutrality, showing evidence of acidification at about 500 m to the east of the Complex. This could be due to the fact that SO_2 is smaller than the particulate matter that contains copper (diameters of <1 µm and <10 µm, respectively) (Environmental Protection Agency, 1996), so that it is capable of being dispersed over greater distances without being deposited on the soil (unless precipitation occurs). This distinguishes the dynamics of deposition for both contaminants and thus affects their spatial distribution on the soil. In addition, this difference in particle size explains why the pH and concentration of Cu in the soil are not statistically correlated. On the other hand, the correlation between pH and distance from the Industrial Complex showed a low R^2 value (R^2=0.14, p<0.05), which indicates that there are other variables, in addition to distance, that influence the dispersion of SO_2. On the other hand, there was no significant correlation between the concentration of copper and the pH of the soil.

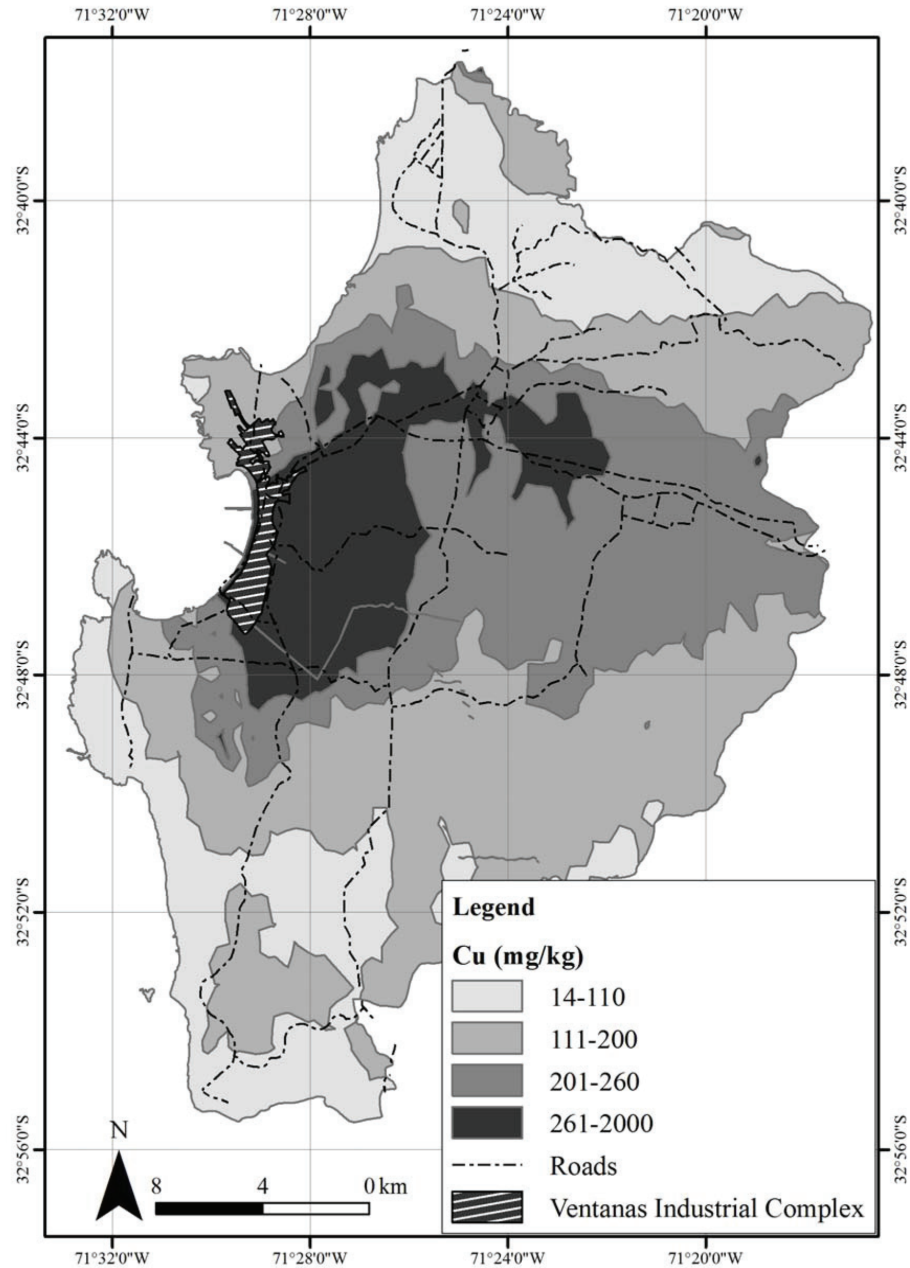

Figure 2. Distribution of total Cu in the soil in the townships of Puchuncaví and Quintero. The ranges were defined using natural breaks.

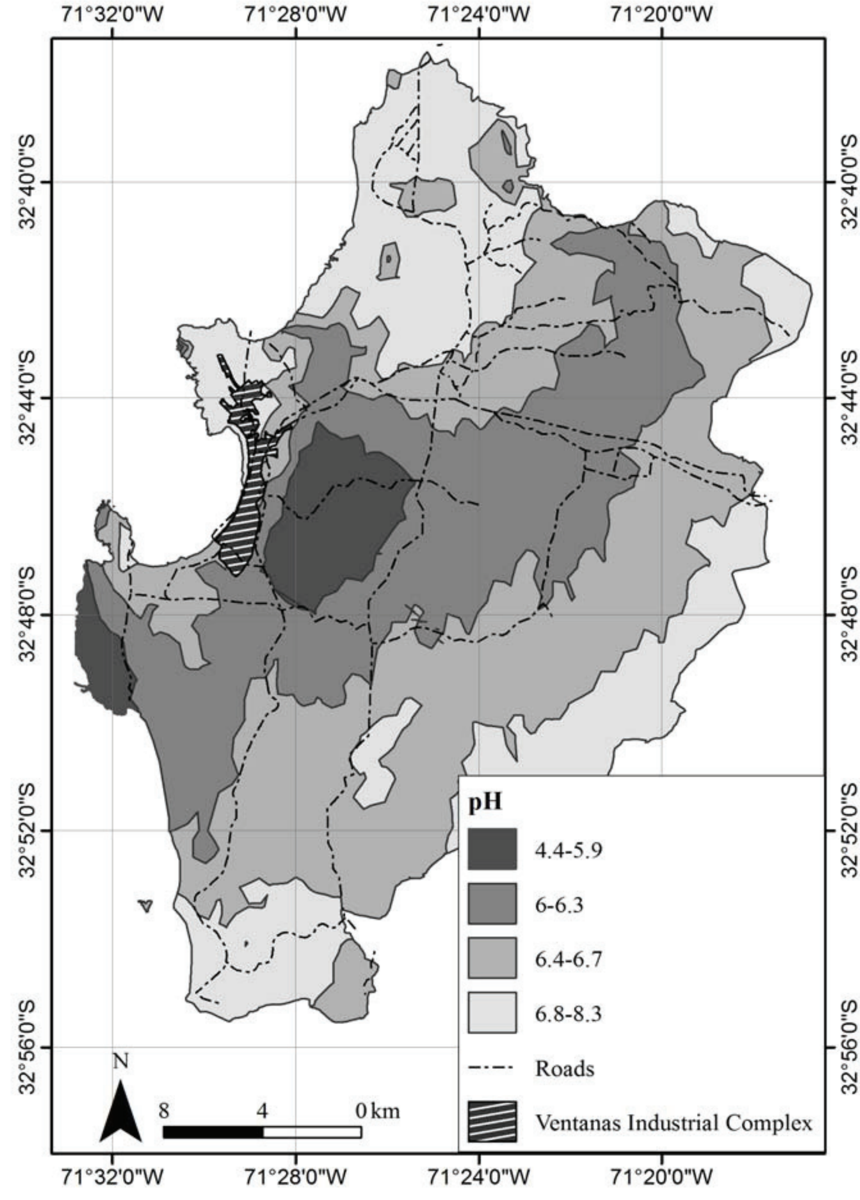

Figure 3. Distribution of soil pH in the townships of Puchuncaví and Quintero.

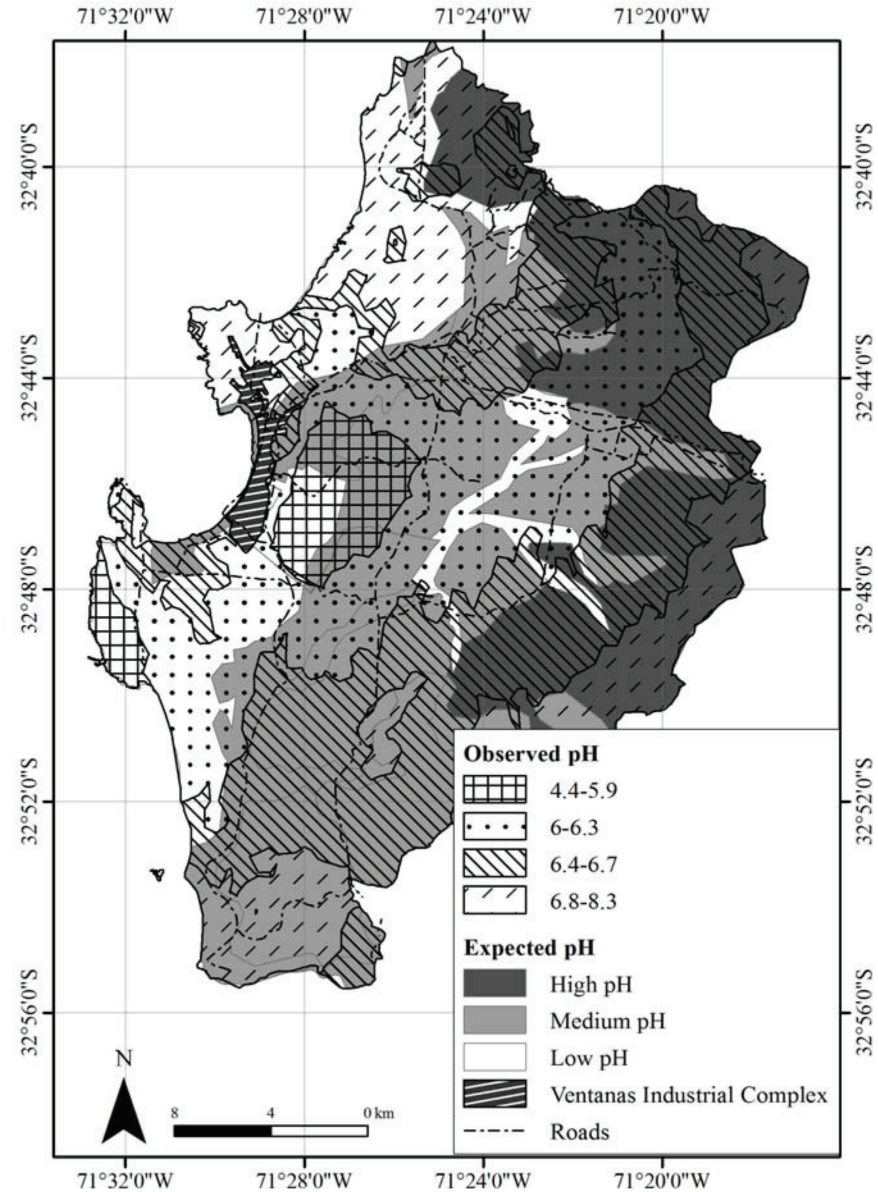

Figure 4. Spatial distribution of expected soil pH, based on lithological units, versus observed pH. Low pH: sand. Medium pH: alluvial, fluvial and colluvial sedimentary sequences, alluvial, fluvial and colluvial deposits, quartz diorites and hornblende-biotite granodiorites. High pH: andesite, basalt, limestone, sandstone.

3.3. Relationship between the soil pH and the lithological units

Lithology affects many characteristics of the soil, among which is the pH (Kram *et al*., 1997; Morales and Viloria, 2005). Specifically, soils that are developed from felsic rocks are more acid in comparison with soils developed from mafic rocks (Brady and Weil, 2002). The lithological units were ranked according to their potential effects on the acidity of the soil. Following this ranking, the lithological unit that could most affect the acidity corresponded to sands (Figure 4). However, no coincidence was observed between the lowest pH range observed in the soil (range of 4.4-5.9). In fact, the unit of sands that comprises the coastal zone of the area of study included the lowest of pH values (pH=4.4) as well as the highest (pH=8.4). Thus, the actual distribution of acidity levels in this area is not associated with the fundamental lithological characteristics of this territory, rather, that it is related to the local and regional meteorological conditions and the levels of emissions.

4. Conclusions

The use of geostatistical tools made possible to generate maps based on the continuous distribution of Cu and pH in the soils in the townships of Puchuncaví and Quintero. The results demonstrated that the distribution of these variables is related to the distance from the Industrial Complex and to the direction of the winds. The concentrations of Cu and acidity are higher in the surroundings to the Complex and in the direction of the dominant winds, that is, to the east of the Complex. Although the distributions of both variables were similar, there was no correlation between the distribution of Cu and pH, which could be due to the distinct aerial dispersion dynamics of the compounds, which causes a divergence in their deposition on the soil.

Considering the Cu concentration values in the control sites, 98% of the soils in the area of this study exceeded the Cu values existing at the control sites.

The theory that the acidity of these soils is due exclusively to the lithology can be discarded given that there is no correspondence between the lithological units and the pH distribution.

In summary, the historical emissions produced by the Ventanas Industrial Complex have caused the acidification of the soils and increased their copper content.

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