Geostatistical space-time interpolation of Cu in mosses using local distribution interpolation

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Abstract

The use of bryophytes to monitor heavy metals allows comparisons over time and space, including the preparation of regional maps and detection of major sources of contamination. Geostatistics allows to characterize the spatial-temporal dispersion of natural resources, and is an important tool for environmental management.

The main objective of this study is to produce an indicator of spatial and temporal variation of atmospheric deposition of Cu in biomonitors based on space-time interpolation by indicator kriging. In this paper, we propose a method to evaluate the evolution of air quality based on estimated local distribution functions instead of comparing the average values estimated at each point on the work area.

The method of interpolation of spatial and time, through the indicator kriging , proved to be a method with good results, because it allows knowing the time evolution in more detail. The approach adopted in this work is extremely important to detect sources of local pollution.

Keywords: biomonitoring, bryophytes, geostatistics, spatio-temporal interpolation, trace metals.

1. Introduction

The Biomonitors use of have proved to be a valuable and cost-effective method to assess air pollution, since they were first used in late 1960 is well known the ability of bryophytes to retain and accumulate metal ions, from the atmosphere. Bryophytes have a simple structure, no walls or cellulose cutinized can absorb water over the entire surface. The ease of ion exchange between the constituent's leads to these biological elements accumulates more metal ions than vascular plants. The bryophytes are the second most numerous phyla of land plants, after the angiosperms, and about 16,000 species (Hawksworrth et al., 1995). The plants are usually green and small and integrate, in general, three main groups: hornworts, liverworts and mosses. Despite some disadvantages identified (no more adapted species in urban environments; compromise or incomplete absorption of some elements with lower affinity; the difficulty of choosing the ideal harvest conditions), a large number of studies have used these organisms for monitoring regional patterns of deposition of heavy metals in the atmosphere (Figueira, 2002). Although mosses not easily calibrate to bulk deposition of heavy metals, and do not integrate atmospheric deposition, they are recommended as a complementary, rather than an alternative technique to conventional analysis of heavy metal deposition (Aboal et al., 2010).

Much has been made in the quantification of heavy metals in Portugal and in Europe through the analysis of bryophytes. In the 90's was a project carried out across Europe "Survey of heavy metal in Europe using bryophytes as bioindicators " (Rühling, 1994, Rühling et al., 1996). made in Portugal where some 180 surveys visited every five years 1990/1992, 1995/1999, 2001/2002 and 2006 in the last campaign surveys were carried out only in the central region. The data obtained in Portugal were integrated into international consortium led by the Council of Ministers of the Nordic countries, involving 28 European countries during the campaign in 1995. This program resulted from a joint project between Sweden and Denmark, started in 1980, which later extended to other European countries (Figueira, 2002). Already in 1985 were used for bryophytes assessment of air quality in Portugal, by calculating the IPA (Index of Atmospheric Purity), based on the richness of lichens and bryophytes (Sérgio and Sim-Sim, 1985). Since 2000, a survey of bryophytes at the European level has been coordinated by the ICP (International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops), (Harmens H. et al., 2010).

Besides measuring network in bryophytes, other network measures the atmospheric deposition of heavy metals called EMEP (Cooperative Program for Monitoring and Evaluation of Long Range Transmission of Air Pollutants in Europe), EMEP measuring the concentrations of heavy metals in air and precipitation. As the EMEP network covers only a limited part of Europe, the models with mosses are used to predict levels of deposition to areas not covered by the measuring stations (Thöni et al., 2011).

Copper is known to cause pulmonary problems in mice by stimulated sensory neurons via a direct activation of the Transient receptor potential A1, a stress sensor protein (Gu and Lin, 2010). Copper in the blood exists in two forms: enzyme-linked ceruloplasmin (85-95%) and the rest is "free" molecules bound to albumin and small. Copper free toxicity causes , since it generates the reactive oxygen forms such as hyperoxia, hydrogen peroxide and hydroxyl radical. These proteins cause damage to lipids and DNA (Brewer, 2010).

Copper (Cu) is an important and essential element for plants and animals. Exists in the earth crust from 24-55 mg/kg, and in soil 20-30 mg/kg. Copper levels in basaltic igneous rocks are much higher than the granitic rocks and much lower in carbonate rocks (Allowey, 1990). Copper is absorbed or specifically "fixed" in the soil, making it one of the trace metals that move the least. Higher concentrations of Cu in the soil are an indication of organic fertilizers, sewage, sludge and other wastes, fungicides or bactericides. The fly ash from burning coal for electricity generation are also a potential source of pollution of Cu, as well from the burning of wood products, fossil fuels and incineration of waste in urban areas. Chemical fertilizers has rarely 100 mg/kg of Cu, even with long-term use; fertilizers do not contribute substantially to soil contamination with Cu. The highest concentrations of Cu in agricultural soils have been associated with the use of fungicides in orchards and vineyards (Allowey, 1990).

The heavy metals may cause hazard effects to human health, because they tend to accumulate in the human body. Occupational exposure is also an important factor that should be taken into account. During the last decade, the health effects caused by air pollution are studied more in developed countries, the monitoring data are most needed in those countries, in order to serve as thresholds configuration (Kampa and Castanas, 2008).

The use of bryophytes in monitoring heavy metals allows comparisons over time and space including the preparation of regional maps and major sources of contamination detection (Aboal et al., 2010). Although the spatial representativeness of samples of bryophytes has been examined in several studies to date, little attention has been given to the temporal representativeness of the results (Boquete et al., 2011). This study wants to reinforce the importance of temporal analysis of the concentrations of heavy metals in bryophytes.

The study by Thöni et al., “Temporal trends and spatial distribution of heavy metal concentrations in mosses in Bulgaria and Switzerland: 1990-2005” confirms that the deposition of heavy metals in bryophytes is a suitable method to detect temporal trends. The big advantage of using spatial-temporal analysis is to monitor temporal trends in order to make decisions that can reduce the concentration of heavy metals in the atmosphere. For example many sources of heavy metal emissions in Europe in recent decades have been replaced by cleaner sources of emissions, like switching from coal to natural gas use as a fuel source or the elimination of leaded gasoline in many parts Europe. In addition, many local emission sources have been closed since 1990, particularly in Eastern Europe (Harmes et al., 2010).

The method of kriging (Soares, 2006) provides an estimation of the probability distribution function of local, the uncertainty of the estimation, which is an extremely important tool for environmental management, useful for example in studies of contamination of soils and aquifers to meet the spatial behavior and temporal pollutant. Through the kriging indicatrix is possible to obtain the probability of the value at a given point exceed or be less than the cutoff value. Extending this analysis to a set of cutoff values, it is possible to determine the probability distribution function for any point in space-time, thus allowing to determine not only the value at this point, but also the associated uncertainty. One can thus quantify different levels of significance of temporal changes in an environmental contaminant

The main objective of this study is to produce an indicator of spatial temporal variation of atmospheric deposition in biomonitors of Cu determined based on space-time interpolation by kriging indicatrix. In this paper, we propose a method to evaluate the evolution of air quality based on estimated local distribution functions instead of comparing the average values estimated at each point on the work area.

2. Methodology

2.1. Sampling and analytical procedure

This study is based o samples from 145 sites, placed in a 30x30 km grid of mainland Portugal-wide extent, but intensified in large urban and industrial areas to a 10x10 km grid (Fig. 1).

Figure 1- Location of samples.

Samples were collected in background areas located at least 500 m from main roads and 100 m from houses and rural roads, following the guidelines for moss biomonitoring protocol (ICP Vegetation 2005). Four campaigns were performed in the period between years 1990 and 2006. The first campaign took place between January 1990 and March 1992 (183 sites), the second between November 1995 and March 1999 (150 sites), the third between April 2001 and October 2002 (150 sites) and the fourth between March and May 2006, this one covering only the central region of the country (98 sites). For the purpose of this study, we used only those sites with samples in, at least, three different dates, totaling 145 sites. Off these, 48 have also data for a fourth campaign. The pleurocarpic moss selected for the study was Hypnum cupressiforme Hedw., which is ubiquous in the northern part of the country. This moss species was also used in other biomonitoring surveys in both national (Otvos et al., 2003, Thöni et al, 2011) or regional levels (Fernandez et al., 2002; Faus-Kessler et al., 2000). In the event of this species not being available, Scleropodium touretii (Brid.) L. Kock was collected. In a previous study, differences between copper concentration in samples of both species collected at the same site and time, were not significant at $p>0.05$ level (Figueira et al., 2002).

2.2. Statistical and geostatistical analysis

In the present work, we intend to study the evolution of Cu concentration determined with a spatial-temporal approach, supplementing it with the comparison of levels of uncertainty determined from inter-quantiles. The values of all campaigns where joined to a final table dataset with 483 lines and four columns: x and y coordinates, Z (harvest date on the drive days, the first date being considered the first day (09/16/1990)) and Cu value (in mg/kg).

The eleven percentile values (10, 15, 20, 25, 50, 75, 80, 85, 90, 95 and 97.5) were determined and used as a cutoff value of 11 new binary variables, one for each percentile. Values below the value of indicatrix took the value 0 and took up the value of 1.

$$I_k(x) = \begin{cases} 1 \ \text{ se } \ Z(x) > Z_k \\ \\ 0 \ \text{ otherwise} \end{cases} \tag{2.2.1}$$

Where Z_k is the value of percentiles.

Before to the Kriging indicatrix (percentiles), were calculated for different steps of the variogram for ***h*** (vector), based on the set of samples, and adjusted by an attenuated middle curve, due to a reduced number of parameters, (direction, amplitude and variance), which quantified the spatial continuity of *Z (x)* (Soares, 2006).

In this study we used the spherical model (Soares, 2006), which is one of the models used in geostatistics. It is a function that depends on two parameters: a level *C*, the upper limit for which the variogram values tend to increase the values of h, and ***a*** the breadth, the distance from which the values of $\gamma(h)$ stop growing and becomes always constant and equal to a level that is usually coincident with the variance *Z (x)*. The scale measures the distance from which the values of *Z (x)* cease to be related (Smith, 2006).

The spherical model has the following expression:

$$\gamma(h) = \begin{cases} C\left[1.5\dfrac{h}{a} - 0.5\dfrac{h^3}{a^3}\right] & h \le a \\ \\ C & h > a \end{cases} \tag{2.2.2}$$

The structures of continuity of values outside of a given variable are quantified through the variogram indicatrix for any cutoff value.

We conducted in this study, a normal Kriging Indicatrix, to obtain a probability distribution function at each point in space. Kriging is based on a variogram model that reflects the main structural characteristics and homogeneity of the attribute in the area where he would sue.

Although this approach is simple has the disadvantage of not guarantee the order relations the estimated probabilities. In this study the maintenance of relations of order was assured by calculating the arithmetic mean between each pair of values, where found, violation of order relations between the estimated values. The kriging estimator does not guarantee that the estimated values are between 0 and 1, then had to be imposed the condition that the estimated values less than zero takes the value 0 and 1 above, take the value 1.

After the model calculated the probability distribution function through indicatrix, for the set of points *x* in the study area ***A***, can be deduced from that, the set of maps relating to the mean values and uncertainty of the estimation (Soares, 2006).

At each point *x* the estimated average value was obtained by:

$$Z^*(x) = \sum_{k=1}^{N_C} f_k(x)\overline{Z}_k(x) \tag{2.2.3}$$

Where N_c is the number of classes (number of indicatrix) of the distribution of frequencies, $f_k(x) = I_k^*(x) - I_{k-1}^*(x)$ the frequency of each class and $\overline{Z}_k(x)$ is the average value of the class.

The uncertainty associated with each estimated average value, measured by the variance of each probability local distribution function was obtained by:

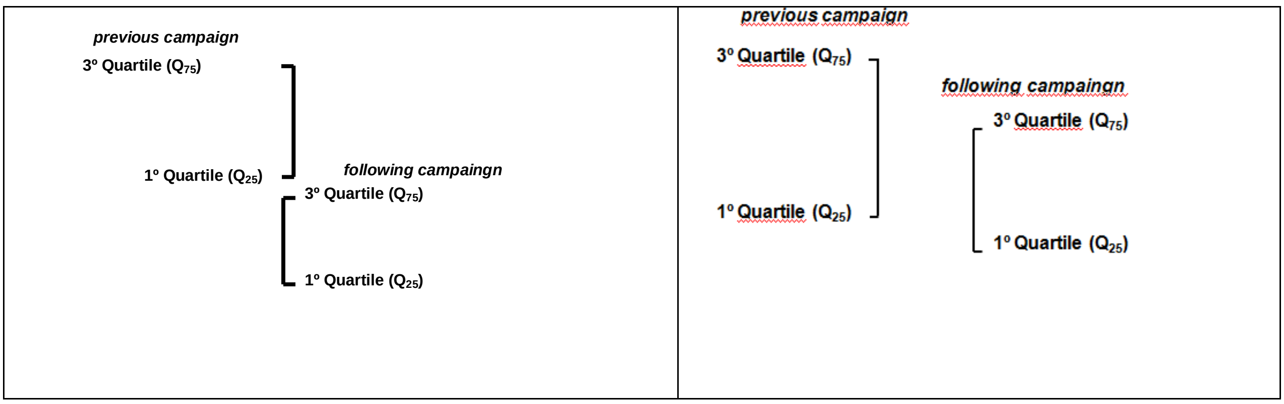
$$\sigma^{*2}(x) = \sum_{k=1}^{N_C} f_k(x)\left[\overline{Z}_k(x) - Z^*(x)\right]^2 \qquad (2.2.4)$$

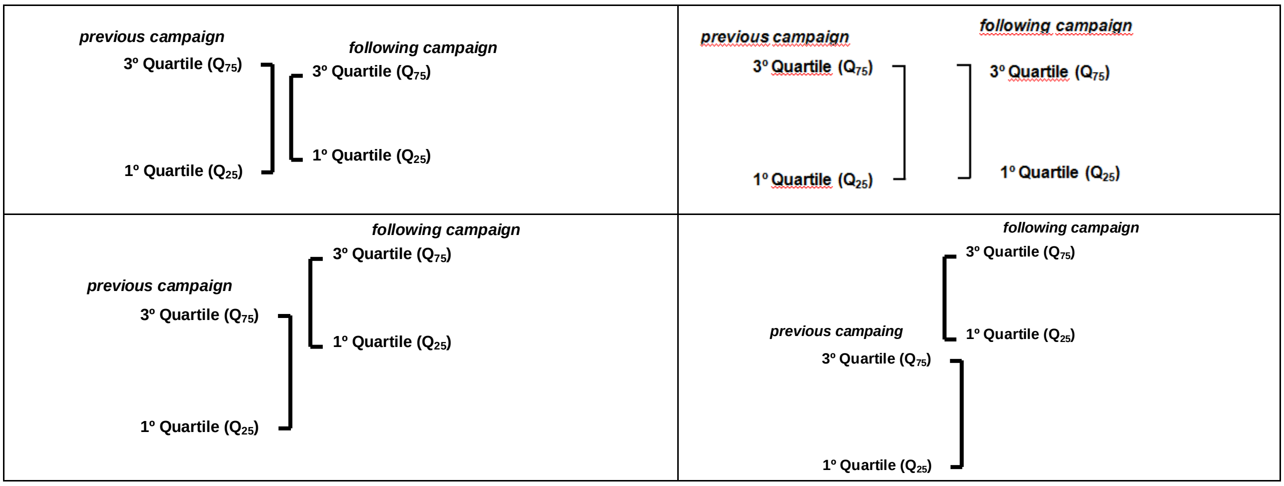
For data analysis in time, we used a step equal to 180 days, resulting in 35 blocks. The comparison was made in blocks (3, 15, 25 and 33), these dates correspond roughly to the average performance of campaigns referred to in Section 2.1, considering the first day as the day of harvest of the first campaign (16/09/1990) .The temporal evolution of air quality based solely on comparison of mean values estimated at different instants of time can lead to wrong conclusions because it does not take into account the uncertainty affecting the estimation of those values. In this paper, we propose to compare the evolution of air quality is done by comparing an inter-quantile instead of the central points of local distribution of probabilities (estimated average). We used two uncertainty intervals:

- Interval center that includes 50% of values between the first quartile and 3rd quartile (Table 1);
- Interval center that includes 95% of the values between the percentiles 2.5% and 97.5% (Table 2).

In order to build a simplified spatial representation of the evolution of Cu concentration, over time and compare the results of campaigns, one for each of the situations described in the preceding paragraphs were created six classes. Classes for the central range which includes 50% of values (inter-quartile range) are shown below. The first class the following campaign means that the value of the third quartile is below the first quartile of the previous campaign. In the latter class, the value of a quartile of the following campaign is higher than the third quartile of the previous campaign.

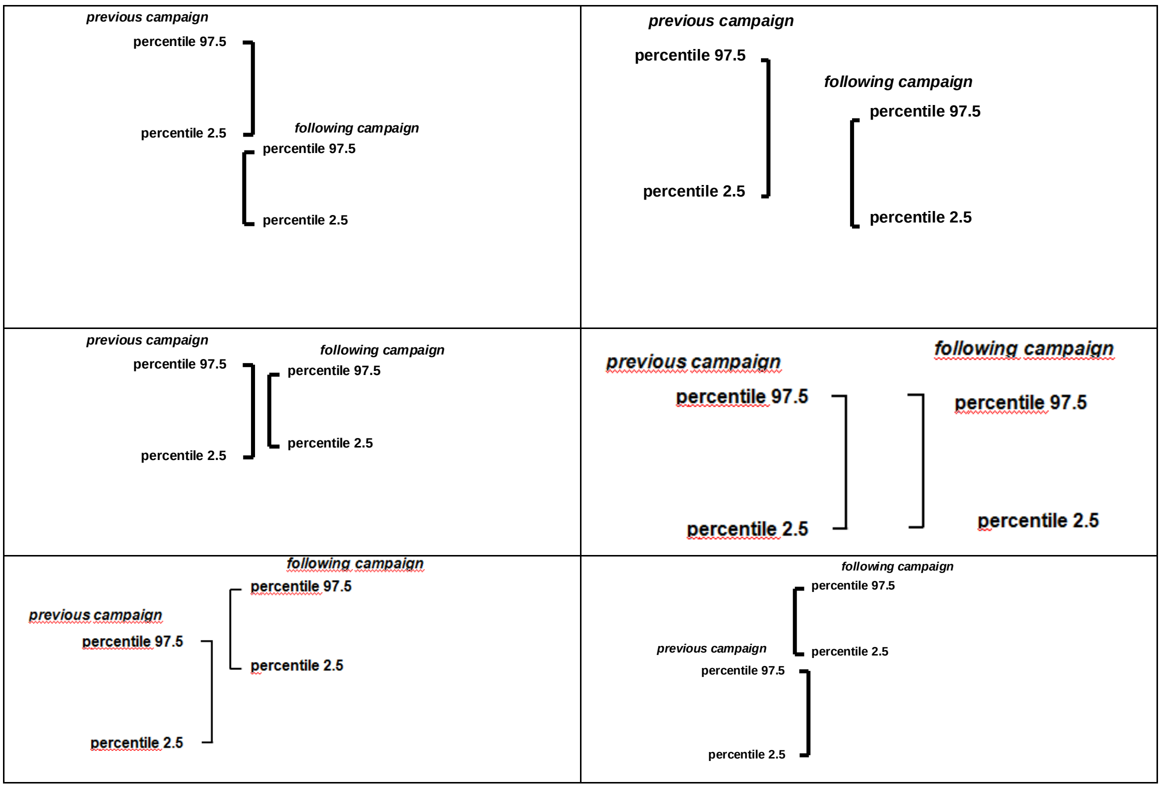
Tabela 1- Uncertainty ranges for the inter-quartile range.





Below are listed the classes of variation for the range that includes central 95% of the values between the percentiles 2.5% and 97.5%. The first class the following campaign means that the 97.5 percentile value is below the 2.5 percentile value of the previous campaign. In the last class, the 2.5 percentile value of the following campaign is above the 97.5 percentile value of the previous campaign.

Tabela 2- Uncertainty ranges for the range between 2.5 and 97.5 percentiles.



The histogram, variogram and kriging were made in GeoMS. For the outputs of the GeoMS were observed in ArcMap 10, it was necessary to build a Java program that converts files to output GeoMS in asciigrid. Asciigrid files can be observed directly in ArcMap, was used for this one python script in order to construct the classes running this on the ArcMap 10.

3. Results and Discussion

3.1. Spatial distribution of Cu

The Cu has an average concentration of 7.93 (mg/kg), with a variation of 42.89. The minimum value recorded is 0.40 (mg/kg) and a maximum of 80.36.
Table 3 shows the cutoff values for the 11 percentile.

Table 3- Percentile values (mg/kg).

Percentile	0.10	0.15	0.20	0.25	0.50	0.75	0.80	0.85	0.90	0.95	0.975
Cutoff	3.530	4.000	4.150	4.700	6.230	9.000	10.120	11.000	13.000	16.820	23.950
Probability	0.101	0.151	0.201	0.251	0.499	0.731	0.799	0.839	0.892	0.948	0.973

3.2. Maps of average concentrations of Cu

In figures 2a, 2b and 2c, we present the maps of spatial-temporal interpolation of Cu concentration, on three dates, corresponding to the cut-off dates for each of the sampling campaigns (blocks 3, 15 and 25 in the time dimension). The values of Cu were obtained from the local distributions estimated by the spatio-temporal kriging of kriging indicatrix (see equation 2.2.3). The fourth campaign (block 33), took place only in the central zone and is shown in figure.2d. The data obtained by this method appear to be consistent with data published in reports of their campaigns.

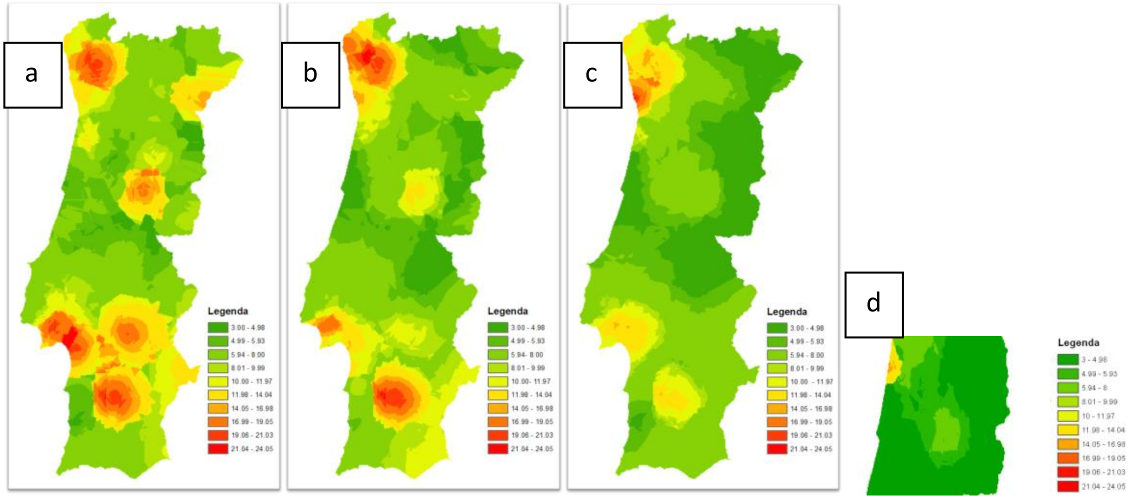


Figure 2- a: Cu values obtained by interpolation space-time by spatio-temporal kriging indicatrix in first campaign; b: second campaign; c: third campaign; d: four campaign.

Comparing the results shown in Figure 2a, with data published in 1993, corresponding to the first campaign (Sergio et al., 1993) shows that they are consistent. The highest values occur in the Douro area probably by the use of silver-rich copper the treatment of vineyards. They are also found in elevated areas of mines and area of Lisboa-Setúbal in the latter may be due to the fact that the existence of Porto de Setubal mining and metallurgical industry exists in Barreiro and Seixal. Industrial activity is also pointed as the main cause for the appearance of high values in the area between Porto and Braga.

Also in figure 2b and compared with published results (Sérgio et al., 2000) the area of the Douro Litoral, Minho and Alentejo are the ones with higher values. Although if there has noticed a general decrease. In figure 2c is visible to the reduction of Cu that can occur due to the fact that they have taken measures to reduce environmental impact in the mines for example EXMIN (Company and Industry Services Miners and Environmental, SA), the public company has the concession rights of the recovery program of the Portuguese mining areas since 2001.In the figure 2d there is a greater amount of Cu concentration in the area of Estarreja probably due to the existence of a larger industrial activity in that area.

3.3. Estimation uncertainty

The figures 3a, 3b, 3c and 3d represent the uncertainty of the estimate made in the previous point, already was mentioned in this paper that the maps for the estimation uncertainty (see equation 2.2.4) can be obtained after calculating the model function probability distribution by kriging of indicatrix.

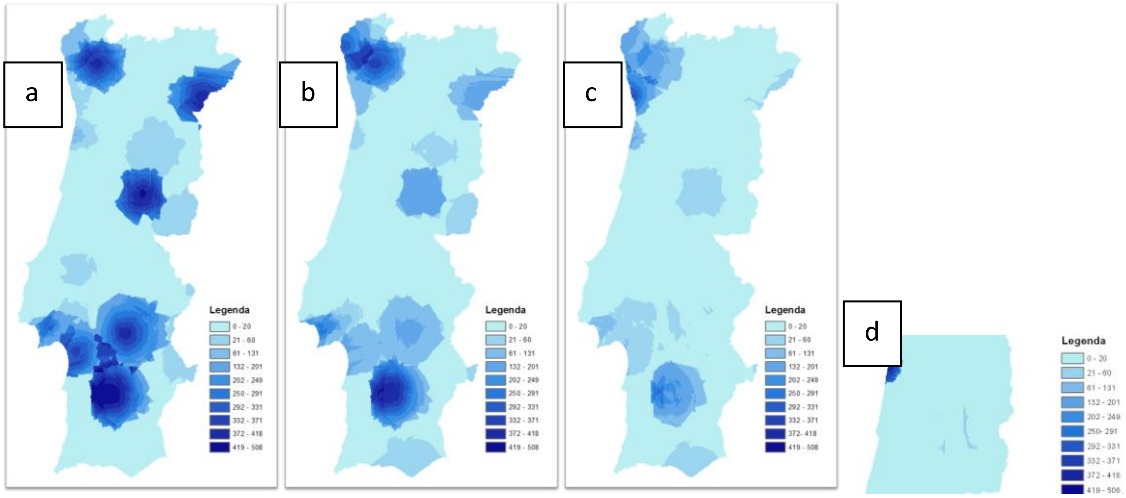


Figure 3- a: Uncertainty estimation of the values of Cu in first campaign; b: second campaign; c: third campaign; d: four campaign.

How can we check the values of greater uncertainty correspond to where the Cu concentration is higher, as discussed in Section 3.2. This is because the concentration difference between two nearby points is very large, i.e., the existence of sites with high levels of Cu close to the places with low value, this implies a greater variance.

3.4. Temporal evolution of the concentrations of Cu

Six classes were created as shown in 2.2, in order to simplify the spatial evolution of Cu concentration over time. Figure 4a shows the difference in mean values of Cu, estimated in 3.2, between the first and second campaign. Figures 4b and 4c makes the analysis of the spatial evolution between the first and second campaign using the uncertainty intervals. Figure 4a shows that the region of Aveiro and Douro Litoral values decreased significantly between the first and second campaign (blocks 3 and 15), in opposition in the region of Sines found a dramatic increase as well as in the Algarve and Minho and also in the central zone.

When we analyze the results obtained with the classes of uncertainty measured by the range of 50% of core values (Fig. 4b) we can see more detail what truly happened over time noting what has been seen in figure 4a, the region of Sines we get higher values, i.e. values of Cu concentrations of the second campaign are all above the third quartile of the first campaign (class 6) in the region of Aveiro values of Cu concentrations of the second campaign are all below the 1st first quartile of the campaign (class 1). Looking at figure 4c, corresponding to classes with uncertainty measured by the range of 95% of the core values we see that the places where there had been a large increase and where there had been a large decrease disappeared, because, we represent 50% of values for 95 %, the range of values increased.

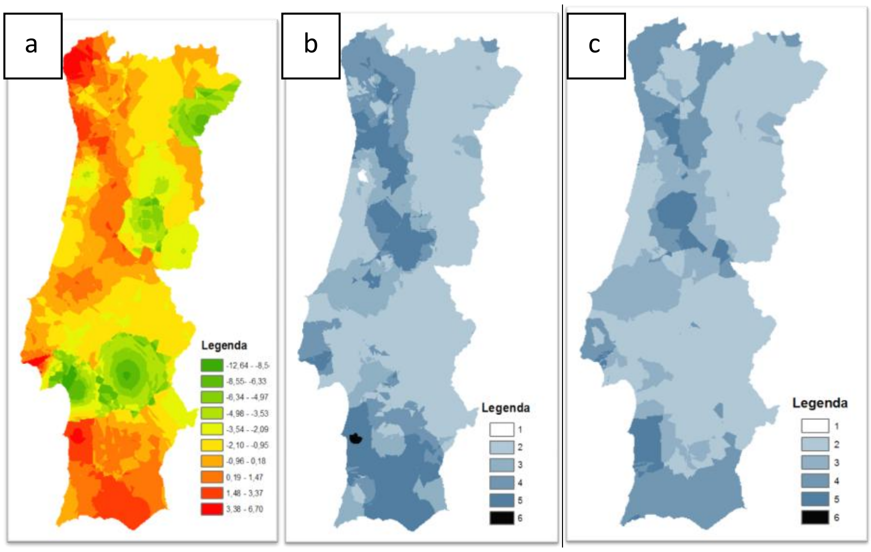


Figure 4- a: Differences in mean values between the first and second campaign; b: Classes with uncertainty measured by the range of 50% of core values between the first and second campaign; c: Classes with uncertainty measured by the range of 95% of core values between the first and second campaign.

Figures 5a, 5b and 5c, compared to the third campaign with the second blocks (25 and 15). Figure 5a shows the difference in mean values of Cu concentrations estimated in 3.2, in the figures 5b and 5c perform the analysis using the spatial evolution of the uncertainty intervals.

In figure 5a there is a general reduction of differences in mean values of the concentration of Cu compared with the figure 4a. When we look at figure 5b refers to classes with uncertainty measured by the range of 50% of core values is notable increases occurring in the area of Trás-os-Montes, as shown in table 2 class 5 indicates that the 75 percentile of the third year is greater than the 75 percentile of the second campaign. The fact that this increase is found, you may have to do with the construction of the A24 motorway linking Vila Real and Chaves, which started construction in 1995.

Figure 5c although classes of uncertainty are measured by the range of 95% of core values, you can also see a greater increase in the amounts of Cu in the first campaign for second in the region of Trás-os-Montes, as shown in figure 5b .

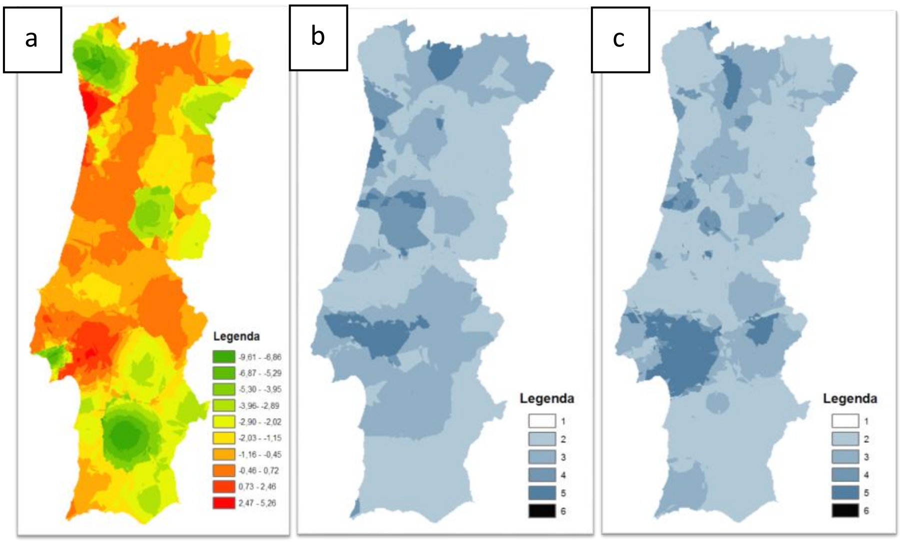


Figure 5- a: Differences in mean values between the second and third campaign; b: Classes with uncertainty measured by the range of 50% of core values between the second and third campaign; c: Classes with uncertainty measured by the range of 95% of core values between the second and third campaign.

Finally, comparing the fourth with the third campaign (blocks 33 and 25), there seems no significant differences in Cu in the central zone, where only held the fourth campaign. In figure 6a we see a greater difference in mean values of Cu concentrations in the area of Estarreja, when we look at the classes with uncertainty measured by the range of 50% of core values (Fig. 6b) and the range of 95% of core values (Fig. 6c), there seems no significant differences in the central Cu. Figure 6c although classes of uncertainty are measured by the range of 95% of core values, you can also see a greater increase in the amounts of Cu in the first campaign for second in the region of Trás-os-Montes, as shown in figure 6b .

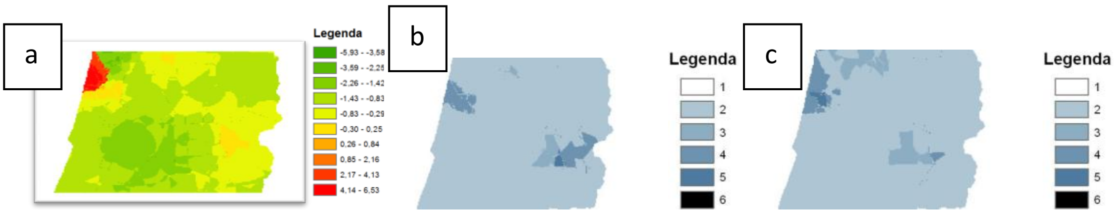


Figure 6- a: Differences in mean values between the third and fourth campaign; b: Classes with uncertainty measured by the range of 50% of core values between the third and fourth campaign; c: Classes with uncertainty measured by the range of 95% of core values between the third and fourth campaign.

3.6. Advantages of the methodology used in relation to a common approach to kriging standard

The method of interpolation spatial-temporal kriging of indicatrix used in this paper had advantages over an ordinary kriging. Allows make estimates of the probability distribution functions of local, being a good method when the histograms exhibit large asymmetry,and also to evaluate the uncertainty. The uncertainty of the estimation obtained from the model probability distribution, is an extremely important tool for environmental management.

Through the kriging indicatrix, is also possible to obtain the probability value at a given point exceed or be less than the cutoff value (indicator), as shown in this study.

The Cu concentration Kriging of spatio-temporal indicatriz maps reflect not only the spatial but also temporal integration obtained by modeling the variogram in this dimension, which is of great importance to good environmental interpretation of the observed contamination for that element. On the other hand, the quantification and representation of the variance estimation allows the identification of areas where there is more rapid changes in space-time, although that does not correspond to areas of infection is highest in absolute terms. Therefore, they are areas that should be given more attention in relation to future changes in the patterns of contamination. Finally, the indicator in classes of varying levels of contamination in the values of Cu are a simple tool for spatial analysis of variations over time and could be a risk indicator for the evolution of atmospheric contamination of Cu in Portugal.

4. Conclusions

This study showed how the indicatrix kriging may be useful to calculate the probability distribution functions of a local data set. As we have seen the data obtained are consistent with previously published without the indicatrix kriging. Kriging also allows indicatrix create maps of uncertainty as shown.

The method of spatial-temporal interpolation by normal kriging indicatrix proved to be a method with good results, because it allows knowing the time evolution in more detail. Through this methodology was possible to represent the evolution of air pollution space-time Cu in Portugal over the past 20 years, levels of variation in space-time and creating a risk indicator for the temporal evolution of atmospheric deposition of Cu. The development is consistent with the reality of the country over time in terms of appearance or mitigate sources of infection. The approach adopted in this work is extremely important to detect many sources of local pollution. As stated Thöni et al., the great advantage of using spatial-temporal analysis is to monitor trends over time in order to make decisions that can reduce the concentration of heavy metals in the atmosphere.

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