SALINE VARIABILITY AT THE SOUTH-WEST OF PORTUGAL AFTER KRIGING DATA FROM *RAMALINA* SPP. BIOMONITORS

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Abstract

Sea-salt input over the land masses may have deleterious effects on man-made structures, vegetable organisms (crops and vegetation) and soil/water resources. Recent work has shown the ability of some lichen species to monitor the deposition of airborne salts of marine origin. The atmospheric transport and deposition of sea salts can be assessed by measuring saline elements in lichens growing over coastal areas. The concentration of Cl^- and Na^+ was determined in lichen thalli collected in three different dates on the south-west region of Portugal. The extracellular fraction of Na^+ was obtained by a sequential elution procedure, and Cl^- was determined after leaching samples with water. The dispersion of element grades in the area was studied through geostatistical analysis. Numerical values were estimated by two interpolation methods: ordinary kriging and kriging with an external drift. The latter method used the logarithm of the distance to the coast as an auxiliary variable and yielded more reliable results. Every set of data produced a similar spatial pattern, showing a steep gradient in the first three kilometres from the coast. However, considerable variation can be observed between surveys. The variability of results is interpreted using the precipitation data obtained for the region under consideration.

1. INTRODUCTION

Airborne salinity is one factor that most contributes to accelerating the degradation of materials and the desertification of land, in the latter case namely through salt-assisted deforestation, aquifer contamination and direct soil impoverishment. However, setting up a classical network to monitor deposition rates of saline elements is all but an easy task, due to its installation and operation costs.

The use of lichens as biomonitors has gone through major developments in the past few decades, as a result of advances in the knowledge of uptake and retention of elements by lichens, especially cations. Also, there has been arising an acute environmental conscience, leading not only to an enhanced control of pollutant emissions but also to the assessment of environmental risk factors. There are many examples referring to the application of lichens in the monitoring of air pollution [1-3].

The total concentration of Cl^- and Na^+ has already been measured in lichens growing in coastal areas [4-7]. For both elements, higher values were obtained in sites near to the coast and their concentrations showed a negative gradient with the distance inland. Recent studies with lichen transplants in the south-west region of Portugal achieved a calibration between lichen and physical monitors, for Cl^- and Na^+ acting as sea-salt tracers [8]. These studies also indicate that an essential parameter to be included in any calibration model is some measure of the (wet) precipitation amount. Another calibration study on mine-derived pollution came to the same conclusion [9].

After sampling over a regional area, the use of geostatistical methods for interpolating the grades of saline elements in lichens shows some advantages. These data-driven methods, born as a supporting tool of mineral-deposit evaluation, turned into an important discipline for environment risk assessment in the nineties. The application of geostatistics is based on the existence of some spatial correlation between sampling points: the smaller the distance, the higher the correlation between a variable measured in both locations. This behaviour can be described by the variogram function. The spatial information from the variogram can then be used for estimating the variate in non-sampled points by kriging. Several kriging procedures were developed to meet different needs in estimation, depending on the properties of the variable in hand. Generally speaking, they rule out bias and minimise the residual variance: in this sense, they give optimal results and perform better than other interpolation methods.

Both the ordinary kriging [10] and the kriging with an external drift [11] estimate the unknown variates as a linear combination of the available samples. However, the latter method also conditions the estimation to another (auxiliary) variable, which must have a well-known relationship with the (primary) variable being processed. In the present study, the lichen concentrations of Cl^- and Na^+ in south-western Portugal were estimated by either method for three sampling campaigns (same locations, different dates). The logarithm of the distance from the coast was taken as an auxiliary variable for the external drift procedure. A comparison between the resulting maps as well as an interpretation of the spatial and temporal variation in the lichen concentrations are given herein.

2. MATERIAL AND METHODS

2.1. Field procedures

The study area is located in the south-western part of Portugal, ranging 16 km along the coast and 10 km inland. This is an almost straight, near-flat region wide open to the westerly winds from the Atlantic ocean. The collection of lichens took place in September 1994, March 1995 and February 1996 at an average of 69 sampling sites, allowing for minor variations between campaigns. Samples of *Ramalina canariensis* Steiner were collected; whenever unavailable, other lichens of the same genera were selected.

2.2. Laboratory procedures

Surface chloride was obtained by shaking *ca.* 50 mg of lichens twice in plastic flasks with 10 ml deionised water. The weight of each sample (dry weight) was determined after drying at 80°C for 16 h. Chloride was measured by mercurimetric titration [12].

The method for assessing the extracellular sodium followed the sequential elution technique by Brown and Wells [13], with some modifications. Prior to elution, complete thalli (about 50 mg) were stored for 24 hours in a high-humidity chamber. The extracellular fraction was obtained by shaking samples in two plastic flasks with 10 and 5 ml of $NiCl_2$ (20 mM) for 40 and 30 minutes, respectively. Through this procedure, all extracellular ions (on the surface, in intercellular spaces and bound to the cell wall) are removed into the nickel solution. Samples were dried at 80°C for 16 h before taking their dry weight. Sodium concentration was determined by atomic absorption spectrophotometry.

The results are given in micromole per gram dry weight (µmol/g d.w.) of lichen, and they are based on five independent samples for each sampling site.

2.3. Statistical analysis

Continuous maps of chloride and sodium concentrations were drawn for the whole study area by geostatistically processing the discrete field data. Before interpolation, experimental variograms were calculated for the variables $[Cl^-]$ and $[Na^+]$. They are the semi-variance for all pairs of samples as a function of the distance (or lag) between sampling points and thus provide a measure of the spatial dependence between samples. The variogram function of a variable $Z(x)$ is defined as

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} \left[Z(x_i) - Z(x_i + h)\right]^2 \qquad (2.1)$$

where $\gamma(h)$ is the estimated semi-variance for lag h and $N(h)$ is the number of pairs of points separated by h. The variograms for the study variables were determined in the four main directions, which are the parallel and perpendicular to the coast, plus the two half-quarters in between.

Theoretical models of spherical form were fitted to the experimental variograms. The parameters of these models (nugget effect, sill and range) were found by an interactive process and then used in the estimation by ordinary kriging and kriging with an external drift. The former estimator should be used only with stationary variables, *i.e.*, variables that show the same mean and variance for the whole field. However, it can be applied to non-stationary variables in sub-areas of the field where they show stationary behaviour. Should the non-stationarity be described by some well-known process, typified by an auxiliary variable all over the estimation domain, then the inclusion of such an external drift into the kriging algorithm can be a suitable device to overcome the problems caused by a less stringent application of ordinary kriging.

The kriging estimator is given by a weighted linear combination of the available samples:

$$Z^*(x_0)=\sum_{i=1}^{n}\lambda_i Z(x_i) \qquad (2.2)$$

where $Z^*(x_0)$ represents the estimated value, $Z(x_i)$ the value of the variable at location i and λ_i the weights assigned to that location. The kriging estimator must be unbiased, which means null differences between actual and estimated values:

$$E\left[Z^*(x_0)-Z(x_0)\right]=0 \qquad (2.3)$$

Should the variable be stationary, *i.e.*, $E\{Z(x_i)\}= m$ (constant), then the sum of weights must equal one:

$$\sum_{i=1}^{n}\lambda_i=1 \qquad (2.4)$$

This is called the universality condition. The optimal solution is obtained by minimising the estimation variance constrained by the universality condition, as follows:

$$E\left[\left(Z^*(x_0)-Z(x_0)\right)^2\right]\text{min} \qquad (2.5)$$

The kriging system appears as a set of equations

$$\begin{cases}\displaystyle\sum_{j=1}^{n}\lambda_j\gamma_{ij}+\mu=\gamma_{i0}\\ \displaystyle\sum_{j=1}^{n}\lambda_j=1\end{cases} \qquad (2.6)$$

where μ stands for the Lagrange parameter that enables the transformation of the constrained minimisation problem into an unconstrained one, with the estimation variance given by

$$\sigma^2=\sum_{i=1}^{n}\lambda_i\gamma_{i0}+\mu \qquad (2.7)$$

Kriging with an external drift follows the same procedure, but the weights for each location are conditioned to an auxiliary variable as well. Now, let the relationship between $Z(x)$ and the auxiliary variable $Y(x)$ be linear and known for the whole estimation field, that is

$$E\left[Z(x_i)\right]=aY(x_i)+b \qquad \forall i=1,\dots,n \qquad (2.8)$$

where a and b are constants. Using Eq. 2.3, Eq. 2.8 can be rewritten as follows:

$$a\left[\sum_{i=1}^{n}\lambda_i Y(x_i)-Y(x_0)\right]+b\left[\sum_{i=1}^{n}\lambda_i-1\right]=0 \qquad (2.9)$$

This brings about a new universality condition (one for each auxiliary variable)

$$\sum_{i=1}^{n}\lambda_i Y(x_i)=Y(x_0) \qquad (2.10)$$

to be accounted for by the kriging system

$$\begin{cases} \sum_{j=1}^{n} \lambda_j \gamma_{ij} + \mu_1 + \mu_2 Y(x_i) = \gamma_{i0} \\ \sum_{j=1}^{n} \lambda_j = 1 \\ \sum_{j=1}^{n} \lambda_j Y(x_j) = Y(x_0) \end{cases} \tag{2.11}$$

and by the kriging variance as well

$$\sigma^2 = \sum_{i=1}^{n} \lambda_i \gamma_{i0} + \mu_1 + \mu_2 Y(x_0) \tag{2.12}$$

3. RESULTS AND DISCUSSION

Several factors may influence the dispersion and deposition of marine salts on land: the distance from the coast, the altitude and the number/type of natural barriers between the sampling location and the coast, among others. The effect of these factors in the accumulation of saline elements by lichens was ascertained through the correlation between such factors and the concentrations of Cl^- and Na^- in the organisms. Every factor was determined for each sampling point using a digital elevation model of the whole study area as support information. The best correlation

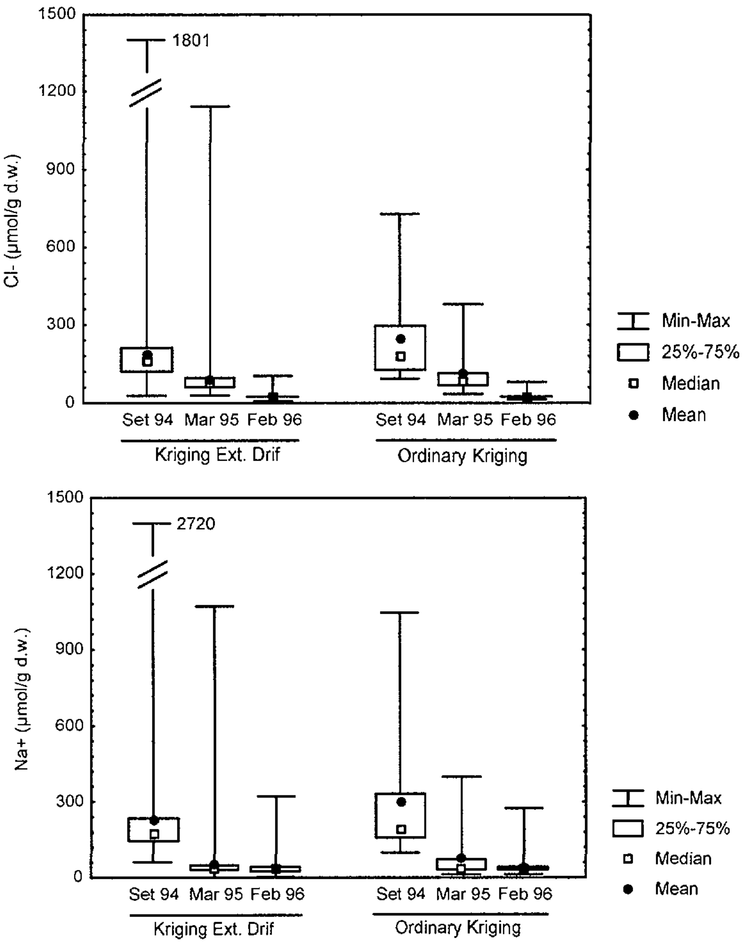

Fig. 1. Statistical parameters for the interpolation results of $[Cl^-]$ *(above) and* $[Na^-]$ *(below), after kriging with an external drift and ordinary kriging.*

was obtained for the natural logarithm of the distance from the coast with coefficients of -0.80 for [Na^+] and -0.75 for [Cl^-], which are significant at $p<0.05$. This logarithmic behaviour was already observed in other studies relating not only to saline elements [4, 5] but to heavy metals as well [3, 14].

The directional variograms show large differences for both elements between the range of the parallel to the coast and the perpendicular one. The former is over three times higher than the latter, indicating the existence of a strong anisotropy, *i.e.*, there is much more continuity along the coastal direction than in its perpendicular.

Statistics for the results of kriging with an external drift and ordinary kriging are given in Fig. 1.

Concerning either element, the amplitude between maximum and minimum is always higher for the external-drift results than for those from ordinary kriging. Kriging with an external drift yielded higher values near the coast and lower values deep inland, due to the inclusion of the logarithm of the distance from the coast as an auxiliary variable. This seems to improve the quality of the estimation, since it was possible to identify a good and comprehensive relationship between the variables being estimated and the auxiliary variable. However, as aforesaid, care must be taken when dealing with an external drift. The relationship between variables should be well understood and physically sound [15], otherwise the results are most likely to turn meaningless.

Considerable variations can be observed on the values of [Cl^-] and [Na^+] referring to different sampling dates. The main reason for this can be the amount of (wet) precipitation observed before each sampling campaign. Figure 2 shows the total rainfall over the three-month period prior to lichen collection. The highest values for both elements were obtained after the first campaign, which took place in the end of a particularly dry summer. Lower values were found for the second and third campaigns, especially for the latter. Both surveys were done after a rainy winter, yet they differ as to the mean rainfall in the three months before lichen collection: the average for the 1996 survey is five times higher than for the 1995 one. The chloride and sodium levels in these lichens thus seem to reflect the variations in the amount of wet precipitation, which is likely to act as a leaching agent rather than an input medium for saline elements. The importance of this factor in the lichen uptake and release of atmospheric constituents has also been addressed by its inclusion in calibration models of lichen contents *versus* atmospheric fluxes [9, 10].

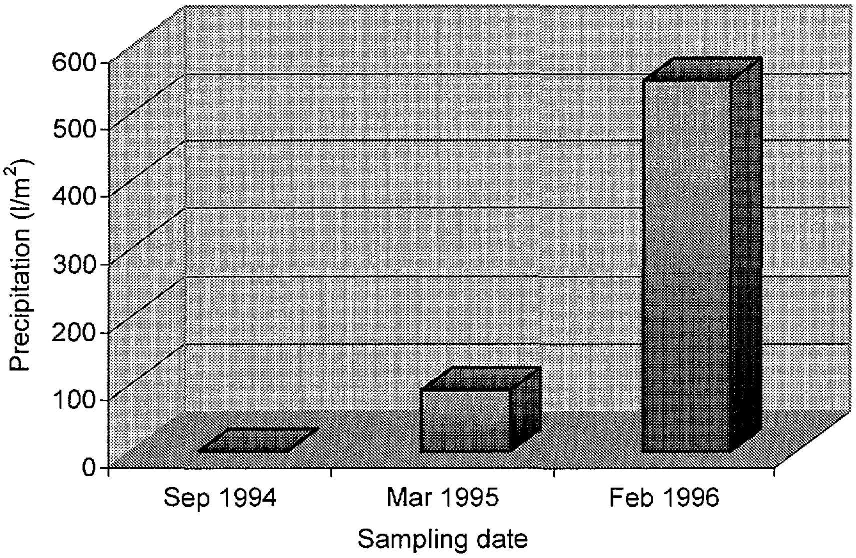

Fig. 2. Rainfall measured in the three-month period prior to lichen-sampling dates.

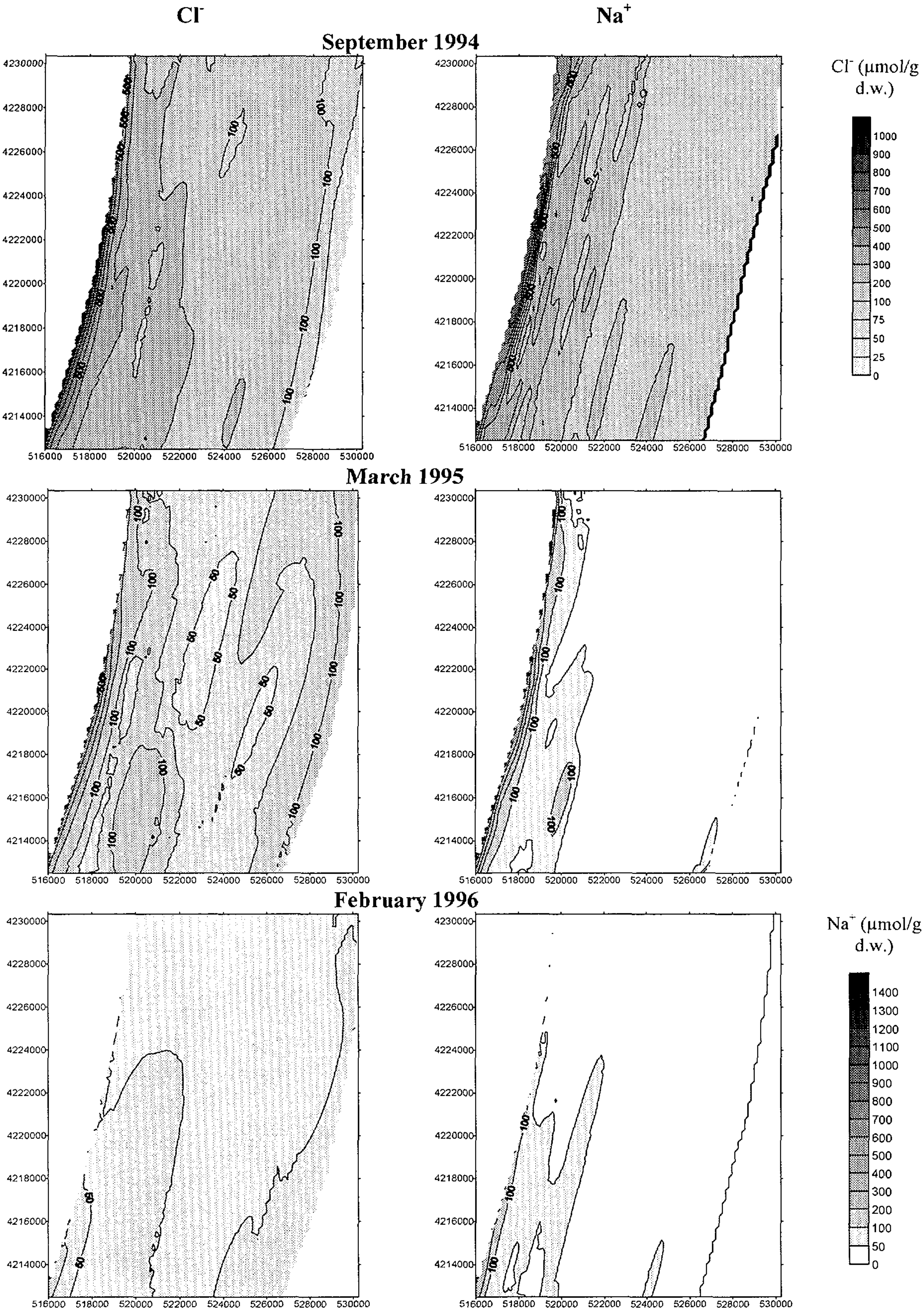

Fig. 3. Maps of $[Cl^-]$ and $[Na^+]$ obtained by kriging with an external driftafter three lichen surveys in south-western Portugal.

The estimation of [Cl^-] and [Na^+] in lichens by external-drift kriging produced the maps shown in Fig. 3. The spatial variation of the estimated values follows a similar pattern for all field surveys: there is always a steep gradient for either element across the first 3 km from the coast. The larger salt nuclei, which are likely to represent the major fraction of the marine aerosol, should be deposited in this area through gravitational settling. Between 3 and 10 km from the coast, the negative gradient is much less pronounced, and little variation can be found for extensive patches within this section. There is also little variation in the north-south direction, though concentration values appear to increase southwards. This is probably due to the existence of a swamp system (Santo André lagoon plus some marshy land), which may act as an entry channel for the maritime air masses over this low-altitude zone.

4. CONCLUSIONS

The concentration of Cl^- and Na^+ in lichens declines with increasing distance from the coast in a logarithmic mode. This behaviour naturally translates into the variograms, which show high anisotropy. Interpolation by kriging with an external drift, using the logarithm of the distance from the coast as a conditioning variable, gives better results than ordinary kriging, especially in areas close to the sea.

In the first three kilometres from the coast, a steep gradient is obtained for either element. Little variation is noticed further inland. This pattern is recurrent in every survey; however, great alteration in the concentration levels is observed from survey to survey. The values show an increasing depletion with the amount of rainfall that occurred before lichen collection, probably due to wash-out effects.

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