SPATIO-TEMPORAL STOCHASTIC MODELLING OF SALINE DEPOSITION MEASURED BY BIOMONITORS

R. FIGUEIRA[1,3], A.J. SOUSA[1], F. DURÃO[1], A.M.G. PACHECO[1,2] and F. CATARINO[3]

[1]CVRM and [2]DEQ, Instituto Superior Técnico, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal

Email: pcrfigueira@alfa.ist.utl.pt

[3]Museu, Laboratório e Jardim Botânico, Universidade de Lisboa, R. Escola Politécnica 58, 1250-102 Lisboa, Portugal

ABSTRACT

The input of sea salt to a coastal environment shows high variability in both space and time domains, hence the estimation of salt-tracing elements in biomonitors should account for either dimension. Furthermore, it is also a non-stationary process, because space variability strongly depends on the distance from the sea. Time variability is mainly dependent on the occurrence of precipitation events, with their leaching effect that causes a decrease of concentrations, and on the period of exposure to the atmosphere in dry conditions. The methodology presented herein deals with the application of kriging with external drift as an interpolation procedure for sodium accumulated by lichens, in a generalised space-time domain. The definition of an auxiliary variable is based on the description of the processes involved in the uptake of sodium from marine origin by epiphytic lichens, through a parametric model that features distance inland, precipitation intensity, and length of the dry period before sampling as major variability factors. Kriging with such an external drift yields better estimates of airborne salinity at ground level than ordinary kriging does, and such an enhanced performance can be checked out from the cross-validation results as well as from an observation of the corresponding, estimated maps.

INTRODUCTION

Inland deposition of sea salt may be seen as a definite hazard to both man-made structures and natural resources. Metallic corrosion and materials degradation at large, as well as negative effects on crops, water and soil quality, are among its notorious impacts in everyday life. In Portugal, most metropolitan and industrial areas are located in the Atlantic littoral, therefore any attempt at serious regional or municipal planning and land management should include saline-risk assessment within their priorities.

Now, large-scale monitoring of inland saltfall by means of physical samplers for wet, dry or bulk deposition would involve high costs related to the installation, maintenance and operation of such devices. An alternative with much lower sampling costs is the use of lichens as saltfall biomonitors. Analysis of contaminants accumulated by these organisms may reflect the surrounding environment, because they lack protective structures in the surface and acquire almost all water and nutrients from the atmosphere. Numerous biomonitoring studies have been reported for the deposition of airborne pollutants like SO_2, trace metals and radionuclides (Castelo *et al.*, 1995; Sloof, 1993; Jeran *et al.*, 1995). Saline elements have also been measured in lichens at the Portuguese coast, and the variability of sea-salt deposition in space or time was ascertained through recurrent sampling. The concentration of chloride and sodium, the main tracers of airborne salinity at ground level (Figueira *et al.*, 1999a), exhibits considerable variation in both space and time, that means a sharp decrease with the distance inland (Figueira *et al.*, 1999b) and a strong dependence on precipitation events prior to sampling dates (Figueira *et al.*, 1999c), respectively.

The decrease in concentration of marine elements with increasing distance from the coast, following an exponential decay, is very much alike what is observed for other contaminants from point sources, like trace metals (Fahselt *et al.*, 1995). The influence of time and precipitation is much more difficult to describe, as the uptake and release of saline elements is a swift process. The concentration of saline elements in lichen samples washed with distilled water takes only fifteen days to get back to natural levels in non-washed samples (Figueira *et al.*, 1998), and removal of such elements by precipitation can easily be observed if the rain episode persists for long enough to cut down on the concentrations in rain-water chemistry, creating an effect similar to distilled water (Figueira *et al.*, 1999b). Any dynamic modelling should access the transients in the process, which means that the sampling frequency should be in the order of a few days. This is clearly infeasible for sampling programs that last for several years, as in the present study, therefore an equilibrium state is assumed for the samples and a static approach is taken for the model.

Conditioning the stochastic estimation of elements to the variability introduced by the above factors, namely the distance from the coast and the extent of precipitation, would allow the production of concentration maps that might better reflect the actual variation observed at ground level. This can be achieved by describing the relationship between the primary variable under estimation (concentration of sodium in lichens) and the factors that explain such variation by means of a stochastic parametric model. In this case, the distance from the coast is clearly space-dependent whereas the precipitation is time-dependent, hence the model accounting for the interaction between each of these factors and the concentration of saline elements must show space-time behaviour. The application of the model would allow the characterisation of the trend inherent in the global process and serve as a support to the estimation through kriging with an external drift, whereby data variability is built into the estimates. The present study uses the former approach to devise a space domain featuring generalised distances in metre-month, and generate maps of sodium concentration in lichens of the *Ramalina* genus that incorporate information on distance, precipitation and dry exposure.

SAMPLING OF LICHENS AND AUXILIARY DATA

Results of three sampling campaigns where combined to give the working data-set used in this study, which refers to the south-western coast of Portugal. The first one corresponds to a monthly sampling program carried out between September 1993 and December 1997 at two locations approximately one and eighteen kilometres from the coast (Figure 1). The second campaign corresponds to samples collected bimonthly at seven sites in a transept at right angles to the coastline, up to thirty kilometres inland. In the third one, a sampling network with 69 sites was defined, and sampling campaigns were performed between September 1994 and December 1997. All samples were epiphytic lichens of the *Ramalina* genus, collected on either pine or olive trees. Extracellular concentrations of sodium were measured in all samples following the method described by Brown and Wells (1988) and Figueira *et al.* (1999a).

Several factors were examined to influence the deposition of sodium on lichens, like distance from the coast, precipitation and number of dry days occurred before the sampling time. It was observed that sodium concentration decreases for higher distances, showing an exponential decay (Figure 2). This pattern is visible for all sampling campaigns and transepts. For precipitation, the general pattern shows that lower sodium concentrations are coincident with rain records (Figure 3). Precipitation values were translated into intensity of rain, here designated as reduced average precipitation (RAP), and calculated for the month preceding the sampling date. Another factor that has also been demonstrated to be important is the number of dry days (without precipitation events) that were observed before the sampling date (Figueira *et al.* 1999d).

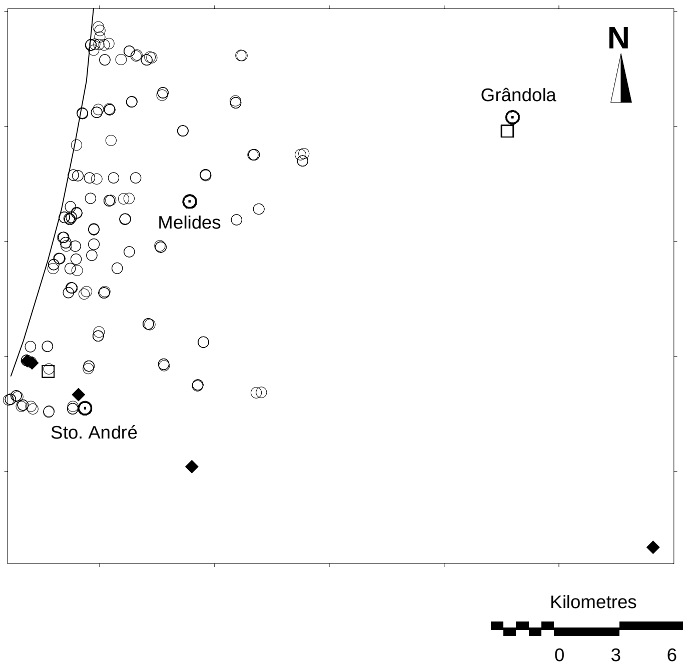

Figure 1. Map of the study area showing sampling locations:

(○) survey; (♦) transept; (□) monthly sampling station.

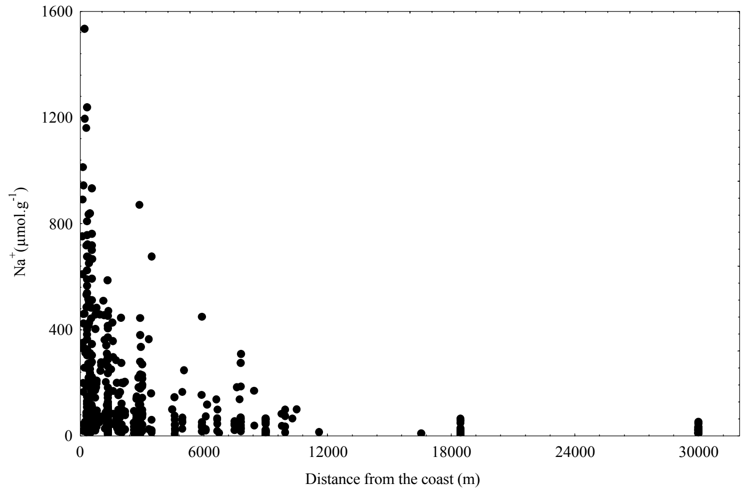

Figure 2. Biplot of sodium concentration and distance from the coast for all lichen samples collected between September 1993 and December 1997.

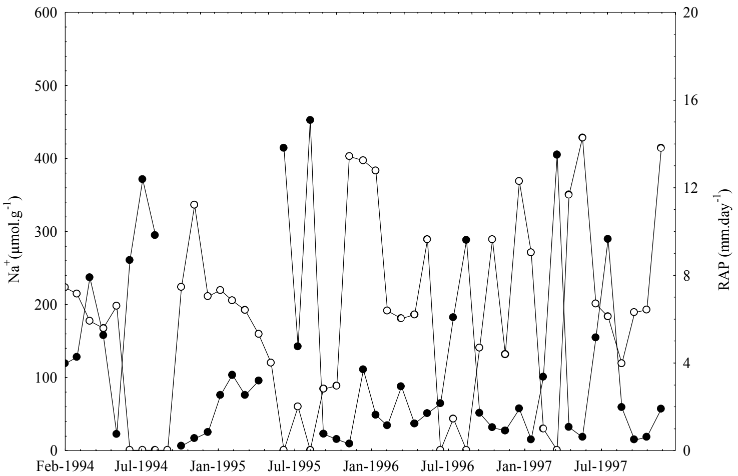

Figure 3. Profiles of sodium concentration and RAP at one kilometre from the coast.

MODELLING THE AUXILIARY VARIABLE

In order to estimate sodium concentrations by kriging with an external drift in a space-time domain, an auxiliary variable was defined as the result of a model including the three factors that better explain the accumulation of this element by lichens, namely the distance from the coast (*dist*), the intensity of precipitation (*rap*) and the number of dry days before sampling (*ddays*). The first factor introduces the spatial variability in the model while the other two are time-dependent. The model combines the effects of factors by a multiplicative model, considering *dist* as main variable in the explanation of the variability, and *rap* and *ddays* as corrective factors to the influence of distance. Thus, the model can be written in the form:

$$Na_{aux}(dist, rap, ddays) = \{[Na_{\max} - Na_{\min}]e^{-K_d dist} + Na_{\min}\}\varphi_1(rap)\varphi_2(ddays) \qquad (1)$$

where

$$\varphi_1(rap) = \{[\varphi_1^{\max} - \varphi_1^{\min}]e^{-K_r rap} + \varphi_1^{\min}\}$$

and

$$\varphi_2(ddays) = \{[\varphi_2^{\max} - \varphi_2^{\min}][1 - e^{-K_D ddays}] + \varphi_2^{\min}\}$$

where Na_{max} and Na_{min} can be considered the maximum and minimum concentration estimated for sodium concentration due to the influence of distance, while φ_1^{max}, φ_1^{min}, φ_2^{max} and φ_2^{min} are corrective coefficients for the intensity of precipitation and number of dry days, respectively; K_d is the distance decay constant and K_r and K_D are rate constants. The influence of *rap* and *ddays* in the model could be more meaningful if information from experimental evidence could be obtained under laboratory or field conditions.

Coefficients determined for the parameters of the model are given in Table 1, and the graph showing the results of the model is presented in Figure 4.

Table 1. Coefficients of the multiplicative model for the estimation of Na_{aux}.

Na_{max}, Na_{min}, K_d	581.412	70.861	0.0015
$\varphi_1^{\max}, \varphi_1^{\min}, K_r$	2.003	0.568	0.5827
$\varphi_2^{\max}, \varphi_2^{\min}, K_D$	1.142	0.598	0.1364

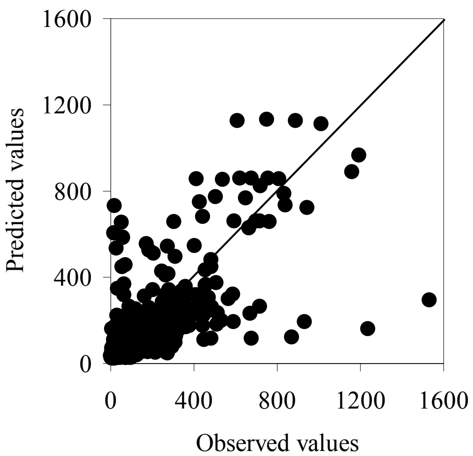

Figure 4. Predicted *vs* observed values of sodium concentration in lichens, determined by the multiplicative regression model.

STRUCTURAL ANALYSIS AND VARIOGRAM MODEL

Saline concentration measured on lichens collected in a coastal region presents naturally strong spatial anisotropy, with lower continuity in the direction perpendicular to the coast. Data values show decreasing variability from the coast inward, which suggests the use of relative variograms that result from dividing the gamma value by the squared local mean. Experimental variograms calculated for the direction parallel (75º) and perpendicular (165º) to the coast are presented in Figure 5, as well as the variogram in time. The spherical models fitted to the variograms considering a space domain with generalised distance in metre-month, are described as

$$\gamma(h,t) = C_0 + C_1\left(sph\left(\sqrt{h_{75}^2\rho_{75}^2 + h_{165}^2\rho_{165}^2}, a\right) + sph(h_t\rho_t, a)\right) \quad h<a \qquad (2)$$

$$= C_0 + C_1 \qquad\qquad h \geq a$$

where h stands for lag, C_0 and C_1 for nugget and spherical model variance, a for the range and ρ_{75}, ρ_{165}, and ρ_t for the anisotropy in 75º, 165º directions and time, respectively.

The nugget effect found in the data can be considered high, reflecting low-scale variability, as well as some variability associated with the living organism and biological processes in accumulation of salt. The parameters found for the spherical model also suggest the existence of geometrical anisotropy, with a high coefficient in the 165º direction (Table 2). The range found for time was 12 months,

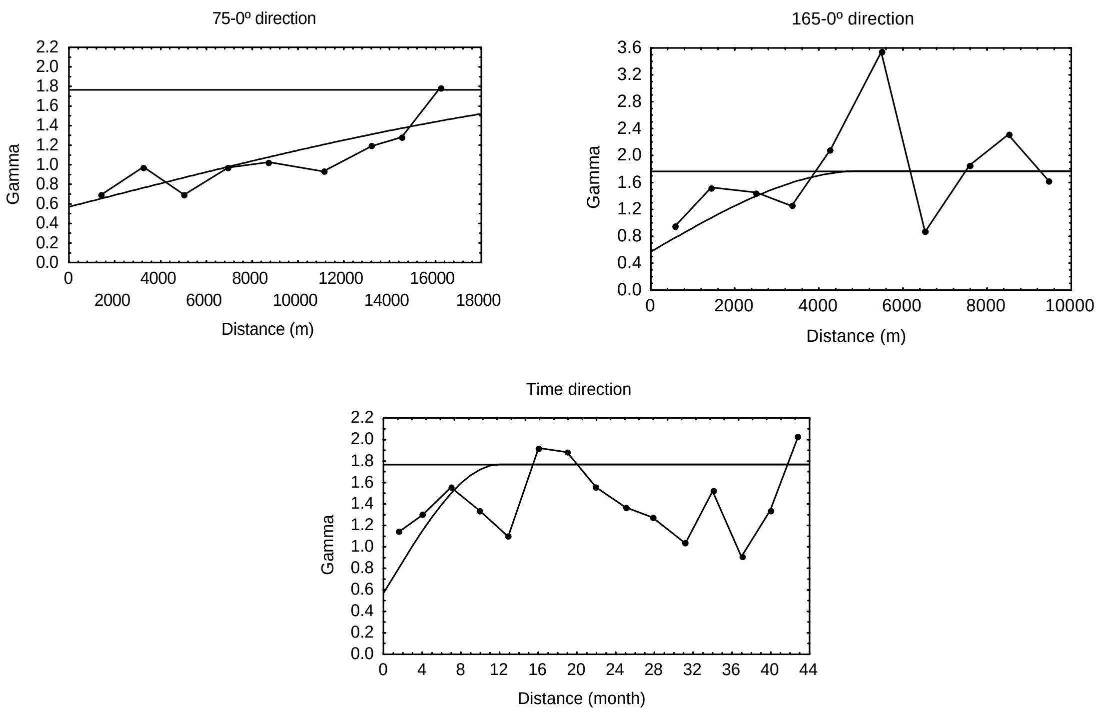

Figure 5. Experimental relative variograms (•) and fitted spherical model for 75º and 165º directions and time. The horizontal line represents the total variance of data.

Table 2. Coefficients of the spherical model fitted to the experimental variograms.

Nugget	Sill	Range	Anisot. 75º	Anisot. 165º	Anisot. Time
0.6	1.2	30000	1	6	2500

suggesting an apparently seasonal effect in the accumulation of marine-derived sodium by lichens. The structural analysis for this variable produced results quite similar to those found for chloride in the same biomonitors (Figueira *et al.*, 1999d).

KRIGING WITH AN EXTERNAL DRIFT

Non-stationary data suggests the use of interpolation methods that could account for the drift observed in the field. The use of kriging with external drift (Wackernagel, 1995) allows addition to the kriging system of universality conditions about an auxiliary variable, known for the entire domain. This is particularly useful in the relationship between the auxiliary variable and actual data can be described in a meaningful way with clear physical sense (Deutsch and Journel, 1992).

The performance of kriging with external drift with evident non-stationary characteristics was ascertained and compared with ordinary kriging, using a cross validation procedure. In these tests, the interpolation was not made by removal of one sample each time, as usual, but removing a range of values corresponding to a particular date, and estimating it from the remainder data. Dates chosen for the test were April 1995, March 1996 and July 1997, all corresponding to sampling surveys and include times where highest and lowest values of sodium concentration were determined (July 1997 and March 1996, respectively). Also a survey with mean values (April 1995) was tested.

Results of cross validation show an increase of the correlation coefficient and an important decrease in residual variance for kriging with external drift outcome, which can be observed for all dates tested (Table 3). It is also apparent that the auxiliary variable, which includes information about the distance from the coast, intensity of precipitation (RAP) and number of dry days before sampling introduces some sensible information into the estimation process, thus leading to better results.

The same can be concluded from an observation of the estimated maps, calculated for the same dates and presented as Figure 6. Maps clearly show a strong decrease of sodium concentration in the first two-three kilometres. The decrease is less marked further inland, showing that the bulk of airborne salinity runs ashore in the first kilometres. This pattern can be found for all dates with no exception,

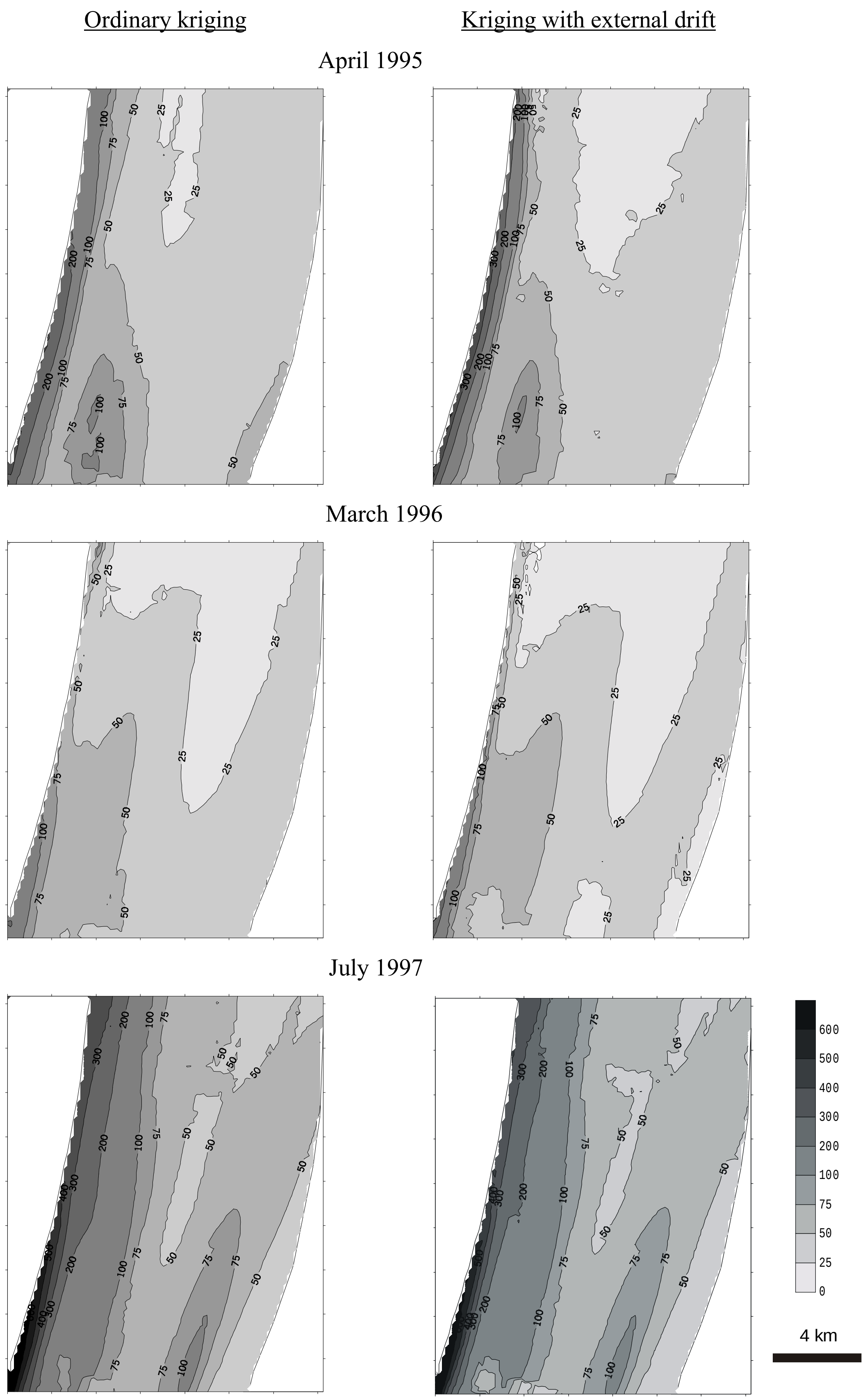

Figure 6. Maps of sodium concentration ($\mu mol\ g^{-1}$ dry weight) in lichens estimated by ordinary (left) and external-drift (right) kriging for different dates.

Table 3. Correlation coefficient (*r*) and residual variance from cross validation tests with ordinary and external-drift kriging.

	OK		KED	
	r	Res. Var.	*R*	Res. Var.
Sodium				
April 1995	0.45	10638	0.77	4654
March 1996	-0.01	5795	0.38	4389
July 1997	0.55	71428	0.68	43313

though great differences can be observed between dates. Results of kriging with external drift always show a steeper gradient with higher maxima near the coast and lower minima inland, reflecting the input of secondary information to the estimation procedure.

CONCLUSIONS

Estimation of sea-salt deposition on lichens, resulting from the dispersion through the atmosphere from sea to inland masses is a problem involving non-stationarity, controlled by some external factors. To deal with this problem, it is proposed to build secondary information into the kriging procedure by means of an external drift. The definition of such an auxiliary information involved the identification of factors that account for the explanation of the variability in the accumulation of saline elements. The main factors thus identified were the distance from the coast, the intensity of precipitation and the number of dry days before lichen sampling, which were used for the definition of an external variable through a multiplicative, parametric model, defined in a generalised space-time domain.

Results of estimation indicate a better performance of kriging with an external drift when compared to ordinary kriging, as ascertained by cross-validation tests. All estimated maps reflect the steep gradient of concentration with increasing distance from the coast, showing that bulk deposition of saline elements is observed in the first three kilometres. Kriging with an external drift yielded higher values in the proximity of the coastline, as well as lower values in the inland areas.

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Email: pcrfigueira@alfa.ist.utl.pt

[3]Museu, Laboratório e Jardim Botânico, Universidade de Lisboa, R. Escola Politécnica 58,

1250-102 Lisboa, Portugal

AUTHOR'S BIOGRAPHY

R. Figueira is graduated in biology by the Faculty of Sciences of the University of Lisbon (1992) and MSc in Georesources by the Technical University of Lisbon (1996). Presently is preparing its PhD in Plant Ecology, under the subject of Development of Environmental Biomonitoring Systems. Actual interests are biomonitoring of air and water pollution using cryptogamic plants (lichens and bryophytes).

Principal recent publications are:

FIGUEIRA, R., SOUSA, A.J., BROWN, D.H., CATARINO, F. & PACHECO, A.M.G. 1999. Natural Levels of Saline Elements in Lichens: Determination of Cellular Fractions and Their Importance as Saline Tracers. *Lichenologist* 31 (2), 183-196.

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