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SPATIAL DISTRIBUTION OF HEAVY METALS RELEASED FROM ASHES AFTER A WILDFIRE

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Abstract. Heavy Metals (HM) in great amounts in soil and water resources can cause coercive effects in the environment and human health. Ash contains high quantities of HM that depend on combusted species, type and part burned and soil characteristics. After a fire, the HM released from ash can lead to a soil solution and water resources contamination. This liberation of HM in solution can be highly variable across the affected area. This work pretends to study the spatial variation of the HM – Aluminium (Al^{3+}), Manganese (Mn^{2+}), Iron (Fe^{2+}) and Zinc (Zn^{2+}) – in a *Quercus suber* and *Pinus pinaster* stand affected by a wildfire in Portugal, applying some interpolation methods. The results showed that on average across the plot, Al^{3+} was the HM released in higher quantities and Zn^{2+} in lower. The higher variability was observed in Zn^{2+} and in Fe^{2+}. The interpolation methods assessed showed that polynomial regression (PR) method was the more accurate to predict the distribution of the HM across the plot. Al^{3+} and Mn^{2+} showed a rise in their concentration from south towards north section of the plot, and Fe^{2+} and Zn^{2+} a decrease from northwest to southeast section of the plot. The liberation of Al^{3+} and Mn^{2+} is related with species burning severity, and Fe^{2+} and Zn^{2+} with plot topography. The fire evolution across the plot and the consequent rising temperatures can have higher impacts than burned species in HM spatial variability. Over time, with the decreasing ash pH, HM will become more mobile and will be released in soil solution, with potential coercive effects in the environment.

Keywords: heavy metals, ash, *Quercus suber*, *Pinus pinaster*, spatial variation, interpolation methods.

1. Introduction

Heavy metals (HM) occur naturally in soil, normally in low amounts, as result of weathering or other pedogenic processes acting on geological bedrock, where soils develop. Some of them are fundamental to plants, however, in excessive amounts (because of their toxic properties) they could have coercive effects on human and ecosystems health (Alloway 1994; van der Voet *et al.* 2000; Vasarevičius and Greičiūtė 2004; Paliulis 2006; Idzelis *et al.* 2007; Baltrėnaitė and Butkus 2007; Jankauskaitė *et al.* 2008; Jaskelevičius and Lynikienė 2009; Jankaitė 2009).

After a wildfire, the remained ash is mainly composed of oxides and hydroxides of base cations, especially calcium, magnesium, and potassium, but also silica and phosphorous, and is characterized by a high alkalinity (Etiegni and Campbell 1991; Khanna *et al.* 1994). Nevertheless, ash contains also variable amounts of HM that could induce toxicity in soil solution and water resources (Ignatavičius *et al.* 2006; Nieminen *et al.* 2005; Pitman 2006). The organic matter mineralization induced by fire, led substantial amount of HM ready to transport, and this could be a source of soil contamination. The amount of HM available and released from ash, depending on species, type and part burned, soil type and temperature reached during the fire (Someshwar 1996; Pereira *et al.* 2009). Hence, after a wildfire, due to different species composition, the amount of biomass and topographic characteristics – that influences burning temperature – the HM released from the ash is certainly much variable.

One of the most important problems in geosciences is the spatial prediction of variables (Babak and Deutsch, *in press*). This problem is known as spatial interpolation and has been studied using several methods. Many conflicting reports have been published, concerning about the use of base statistics to predetermine interpolation methods and their parameters (Zimmerman *et al.* 1999; Robinson and Metternicht 2006). Numerous studies have compared the accuracy of interpolation methods, especially with geostatistical methods (Goovaerts 2000; Schloeder *et al.* 2001; Triantafilis *et al.* 2001; Erxeleben *et al.* 2002; Vicente-Serrano *et al.* 2003; Pardo-Igúzquiza and Chica-Olmo 2005; Diodato and Ceccarelli 2005; Scull *et al.* 2005; Robinson and Metternicht 2006; Simbahan *et al.* 2006; Yilmaz 2007; Luo *et al.* 2008; Xiaowei *et al.* 2008; Yasrebi *et al.* 2009; among others). Also, other studies have been made about the spatial variability of soil properties, with interpolation methods (Goovaerts 1998; Facchinelli *et al.* 2001; Baxter *et al.* 2003; Cetin and Kirda 2003; Castrignano and Buttafuoco 2004; Liu *et al.* 2004; Baxter and Oliver 2005; Corstanje *et al.* 2006; Jalali 2007; Boruvka *et al.* 2007; among others), but only some about the effects of fire (Robichaud and Miller 1999; Gimeno-Garcia *et al.* 2004; Outeiro *et al.* 2008). There is a lack of reports in international literature about the spatial variability of the effects of fire on ash nutrient release. In order to fill this gap, the aim of this study is assess the accuracy of various well-known interpolation techniques for mapping the spatial variability of HM– Aluminium (Al^{3+}), Manganese (Mn^{2+}), Iron (Fe^{2+}) and Zinc (Zn^{2+}) – released from ash after a wildfire in a plot dominated by *Quercus suber* and *Pinus pinaster*.

2. Data and methodology

2.1. Study site, sample collection and laboratory analysis

The wildfire occurred near Lisbon region (Portugal) (Fig. 1) at July 30 2007 and affected an area of ±40, dominated by *Pinus pinaster* and *Quercus suber* trees. Inside this area, we designed a plot with 9x27 m (Fig. 2) where the fire effects were more homogenous and we collected 40 ash samples in soil surface four days after the fire. Coordinates of the sample points were took with GPS. In the studied plot the fire evoluted from west to east.

1 gr of ash of each point were mixed with 40 ml of deionised water (1:40) during 24 hours and then filtered though a Whatman 0.45 μm pore size filter QMA quartz fibre. The solution was analysed by inductively coupled plasma mass spectrometry (ICP-MS) with a PerkinElmer, model Elan-6000 Spectrometer, and by optical emission spectrometry (OES) with the, PerkinElmer Optima 3200 RL Spectrometer.

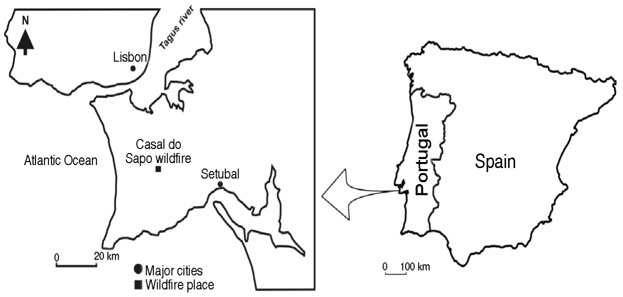

Fig. 1. Location of the wildfire area

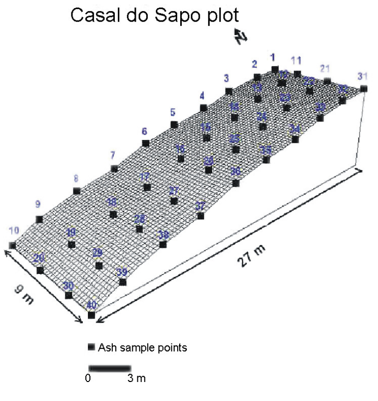

Fig. 2. Plot topography and sample points

2.2. Statistical analysis

To observe the amount and variability of HM released from the ash, we analyzed some descriptive stats (mean, standard deviation, coefficient of variation (CV%), minimum, 25th percentile, median, 75th percentile, maximum, skewness and kurtosis). Before modelling data, we tested if the data followed the Gaussian distribution applying the Shapiro-Wilk test (Shapiro and Wilk 1965) and considering data normaly distributed at $p > 0.05$. If the original data do not respect the normal distribution, we applied a normal logarithmic (Ln) data transformation and tested again if this transformed data followed the Gaussian distribution. Ln transformation is widely applied to normalize positively skewed data sets (McGrath *et al.* 2004). In this study, Al^{3+} (Fig. 3a) and Mn^{2+} (Fig. 3b) followed the normal distribution with the original data and Fe^{2+} (Fig. 3c, d) and Zn^{2+} (Fig. 3e, f) only after the Ln transformation. Therefore, we used to test the performance of the interpolation methods in analysis, the original data of Al^{3+} and Mn^{2+}, and the Ln transformed data of Fe^{2+} and Zn^{2}. This lack of data normality was also found in other studies about soil HM spatial distributions (McGrath *et al.* 2004; Liu *et al.* 2004; Hooker and Nathanail 2006).

2.3. Interpolation methods

Interpolation methods differ in their assumptions, local or global perspective, and deterministic or stochastic nature (Luo *et al.* 2008). To observe the spatial data distribution, we selected several interpolation methods, that use known data values to estimate unknown data values (Yilmaz 2007), Kriging method (K), Inverse Distance Power (IDP), Nearest Neighbour (NN), Local Polynomial (LP) and Polynomial Regression (PR).

K method is a stochastic technique that uses a linear combination of weights at known points to estimate the value at an unknown point and it is very popular in many fields (Surfer 8 Manual 2006; Luo *et al.* 2008). K is regarded as an optimal spatial interpolation method, which is a type of weighted moving average:

$$\hat{Z}(s_0) = \sum_{i=1}^{N} \lambda_i Z(s_i)\,, \qquad (1)$$

where: $Z(s_i)$ is the measured value at the ith location, λ_i is an unknown weight for the measured value at the ith location, s_0 is the prediction location and N is the number of measured values.

IDP method is a weighted average interpolator, and can be either an exact or a smoothing interpolator. Data are weighted during interpolation such that the influence of one point relative to another declines with distance from the grid node. Weighting is assigned to data through the use of a weighting power that controls how the weighting factors drop off as distance from a grid node increases (Surfer 8 Manual, 2006). This method is calculated according to the formula:

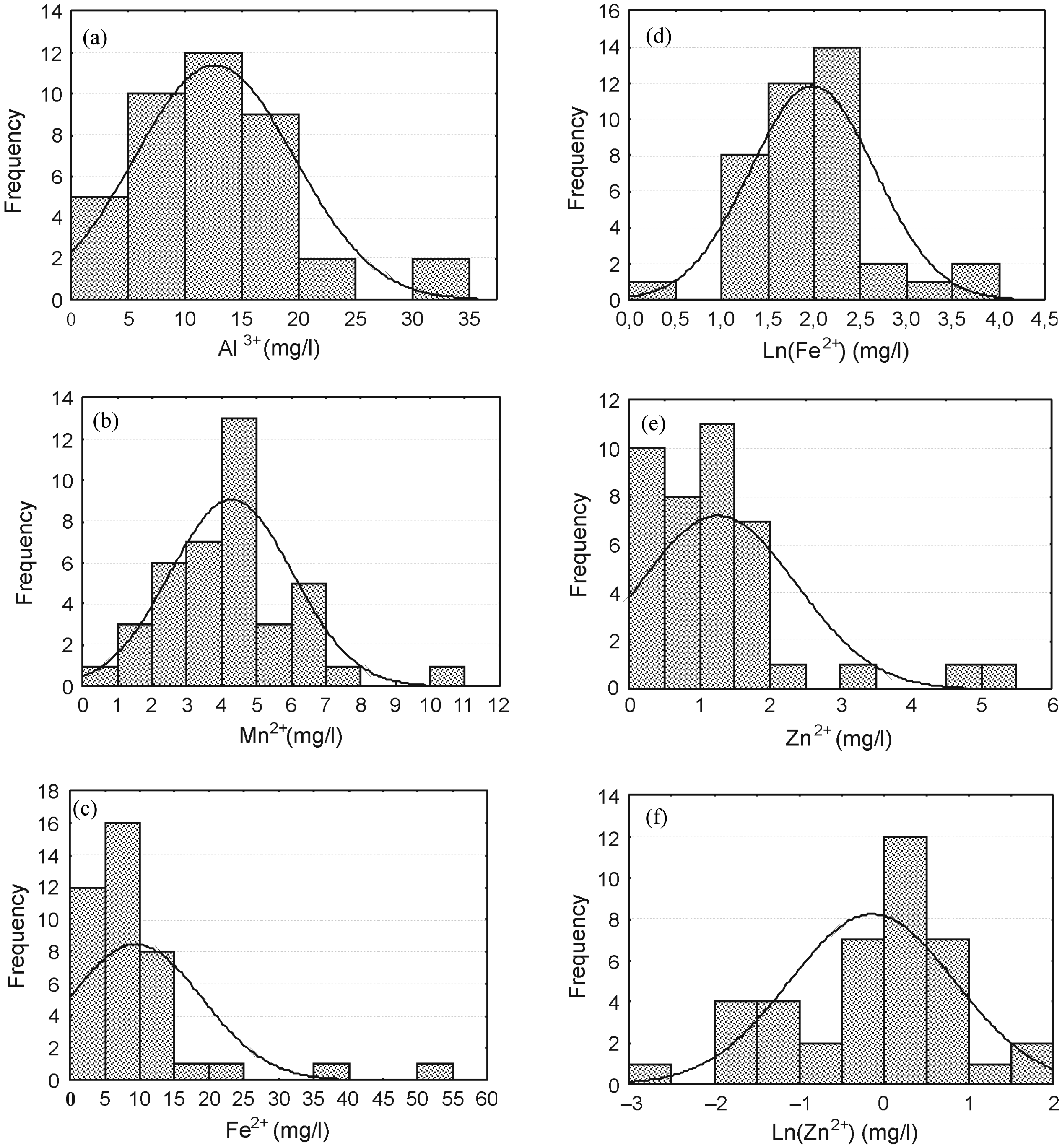

Fig. 3. Histograms of heavy metals released in solution from ash. (a) Al^{3+} (b) Mn^{2+} (c) Fe^{2+} (d) Ln(Fe^{2+}) (e) Zn^{2+} (f) Ln (Zn^{2+}). Data in milligrams per litre (mg/l) ($n = 40$)

$$\hat{Z}_j = \frac{\sum_{i=1}^{n} \frac{Z_i}{h_{ij}^{\beta}}}{\sum_{i=1}^{n} \frac{1}{h_{ij}^{\beta}}}, \tag{2}$$

$$h_{ij} = \sqrt{d_{ij}^2 + \delta^2}\ , \tag{3}$$

where: h_{ij} is the effective separation distance between grid node j and the neighboring point i, Z_j is the interpolated value for grid node j, Z_i are the neighboring points, d_{ij} is the distance between the grid node j and the neighboring point i, β is the weighting power (the *power* parameter) and δ is the *smoothing* parameter.

NN gridding method assigns the value of the nearest point to each grid node. This method is useful when data are already evenly spaced. Alternatively, in cases where the data are nearly on a grid with only a few missing values, this method is effective for filling in the holes in the data.

LP gridding method assigns values to grid nodes by using a weighted least squares fit with data within the grid node's search ellipse. Also is a moderately quick deterministic interpolator that is inexact (Surfer 8 Manual 2006; Luo *et al.* 2008).

PR method is mainly used to define trends in data and it is not really interpolator because it does not attempt to predict unknown Z values. In this work we applied a simple linear surface based on the formula:

$$Z(X,Y) = A + Bx + Cy\,. \tag{4}$$

Cross validation was used to evaluate the performance of each interpolation method. This was achieved removing temporarily one observation at a time from the data set and "re-estimate" this value from the remaining data applying using the alternative algorithms. This procedure was repeated for all observations in data set. The cross validation allows us to assess the quality of the gridding method (Goovaerts 2000; Erxleben *et al.* 2002; Surfer 8 Manual 2006). Is an excellent scheme for solving inconvenience of redundant data collection, and all collected data can be used for estimation (Webster and Oliver 2001). In the cross validation procedure the true values were subtracted from the estimated values. The resulting residuals from this process were evaluated in order to access the accuracy of the methods. This process allowed the mean error (ME) and the root mean square error (RMSE) test statistics to be calculated for each interpolation method considered in this study. The ME and RMSE formulas are:

$$\mathrm{ME} = \frac{1}{N}\sum_{i=1}^{N}[\hat{z}(s_i) - z(s_i)]\,, \tag{5}$$

$$\mathrm{RMSE} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}[\hat{z}(s_i) - z(s_i)]^2}\,. \tag{6}$$

The ME calculates the bias of the model and should be close to 0.Robinson and Metternicht 2006). The RMSE is an indicator of the sensitivity to outliers, identify the magnitude of extreme errors and it is low when there is a central tendency and extreme errors are small (Ashraf *et al.* 1997; Nalder and Wein 1998). RMSE was applied to compare the different interpolation methods by seeing how predicted values are close to observed values. The method with the smaller RMSE is the best predictor. The differences between observed and predicted means were tested with a *t-test* for paired samples, statistically different at 95%. Statistical analyses were performed in Statistica 6.0 (Statsoft, inc.) and interpolation methods tests in Surfer 8.0 (Golden Software).

3. Results and discussion

3.1. Descriptive statistics

The statistical results of the HM released from ash in solution are summarized in the Table 1. We observed on average that Al^{3+} is the ion in higher amount in the solutions and Zn^{2+} the less. The CV% of Fe^{2+} and Zn^{2+} were of 100.53 and 88.80, respectively, and higher than Al^{3+} and Mn^{2+} suggesting a greater spatial variability. The range of Al^{3+} varies from 0.61 to 31.24 mg/l, Mn^{2+} from 0.39 to 10.12 mg/l, Fe^{2+} from 1.63 to 53.55 mg/l and Zn^{2+} from 0.08 to 0.49 mg/l.

3.2. Interpolation methods assessment

Table 2 a, b, c and d presented the results of interpolation tests of HM in study. The results obtained from the cross validation procedure showed that in all methods, the ME was small, and close to 0, especially in PR. It should be noted that the negative ME suggest that the methods of prediction applied in this study overestimate the variables (observed<predicted). We observed this situation in K and LP in Al^{3+}, K and IDP in Mn^{2+}, K, IDP and NN in Ln (Fe^{2+}) and in IDP in Ln(Zn^{2+}).

In all models considered, PR presented the lower RMSE values and NN the higher. This means that the PR is the best method to interpolate these surfaces and NN the less accurate. The results obtained from the *t*-test mean comparison, also revealed that in PR, the observed values and predicted values had lower differences in all HM in study. In opposition, in NN this differences were higher (with exception of Ln(Fe^{2+})). The differences between observed and predicted were non significant at a $p<0.05$ in all considered methods (Table 2a, b, c and d).

The interpolated maps of the most accurate method, are showed in the Figure 4a, b, c and d. We observed that $Al^{3+}$and Mn^{2+}, showed an increasing trend from south part towards north of the plot. In Fe^{2+}(Ln) and Zn^{2+}(Ln) we identified a different trend, from northwest to southeast of the plot. These differences can be a result of the effects of burning temperatures on fire severity, the influence of topography on fire evolution across the plot and how each metal response to fire temperature and severity.

Table 1. Descriptive statistics of the metals in study released from ash. m (mean), SD (standard deviation), Coefficient of variation (CV%), Q1 (25th percentile), M (median), Q3 (75th percentile), S_k (skewness), K_{ur} (kurtosis) and SW (Shapiro-Wilk test). Data in mg/l ($n = 40$)

Metals	m	SD	CV%	min	Q1	M	Q3	max	S_k	K_{ur}	SW
Al^{3+}	12.51	7.01	56.04	0.61	7.79	12.70	16.48	31.24	0.62	0.92	.630
Mn^{2+}	4.25	1.76	41.41	0.39	3.05	4.14	4.95	10.12	0.76	2.22	.151
Fe^{2+}	9.38	9.43	100.53	1.63	4.53	6.36	10.76	53.55	3.44	13.50	.000
Fe^{2+}(Ln)	1.97	0.67	34.01	0.49	1.51	1.85	2.38	3.98	0.79	1.53	.072
Zn^{2+}	1.25	1.11	88.80	0.08	0.49	1.07	1.61	5.33	2.04	5.32	.000
Zn^{2+}(Ln)	–0.16	0.97	–606.25	–2.53	–0.72	0.07	0.47	1.67	–0.57	–0.04	.125

Table 2. Results of the ME and RMSE from cross validation procedure and observed vs. predicted *t*-test means comparison, significant at a $p<0.05$. Al^{3+} (b) Mn^{2+} (c) $Ln(Fe^{2+})$ (d) $Ln(Zn^{2+})$ ($n = 40$)

a)

Method	ME	RMSE	Obs *vs*. pre
K	–0.010695	4.915898	0.991
IDP	0.229910	4,640104	0.817
NN	0.565000	6.161000	0.647
LP	–0.389867	4.742168	0.691
PR	**0.000000**	**4.639950**	**1.000**

b)

Method	ME	RMSE	Obs *vs*. pre
K	–0.008544	1.471181	0.977
IDP	–0.009531	1.336493	0.973
NN	0.245000	1.755000	0.499
LP	0.014692	1.374928	0.958
PR	**0.000000**	**1.188208**	**1.000**

c)

Method	ME	RMSE	Obs *vs*. pre
K	–0.006380	0.513509	0.949
IDP	–0.023276	0.503371	0.821
NN	–0.004397	0.655735	0.972
LP	0.054860	0.513261	0.581
PR	**0.000000**	**0.479035**	**1.000**

d)

Method	ME	RMSE	Obs *vs*. pre
K	0.018829	0.826902	0.910
IDP	–0.030229	0.746002	0.844
NN	0.194576	0.895131	0.307
LP	0.025374	0.750341	0.875
PR	**0.000000**	**0.705427**	**1.000**

The fire severity was higher in the southern part of the plot and lesser in the northern part. This can be a result of the major dominance of *Pinus pinaster* trees in this area (Pereira *et al.* 2008a). Some studies identified that *Pinus* species are more flammable than *Quercus* species (Guijarro *et al.* 2002; Liodakis and Kakardakis 2006), due the higher presence of volatile components (oils) (Dimitrakopoulos and Papaioannou 2001). Nuñez-Regueira *et al.* (1996) observed that *Pinus pinaster* have higher calorific values and as consequence higher flammability. Ubeda *et al.* (2009) founded that at same fire temperatures, the severity is higher in *Pinus* ash in comparison with *Quercus* ash.

The ash produced at higher temperatures or in severe wildfires, have high pH values (Etiegni and Campbell 1991; Khanna *et al.* 1994; Henig-Sever *et al.* 2001) and inhibited the solubility of HM Also, high temperatures of combustion, often observed in wildland fires, produced ash rich in $CaCO_3$ (Ulery *et al.* 1993; Goforth *et al.* 2005; Pereira *et al.* 2008a). This mineral have the capacity of HM sorption in his surface (when in solution) mainly at high pH values (Etiegni and Campbell 1991; Demeyer *et al.* 2001; Chirenge *et al.* 2006, Ettler *et al.* 2006; among others). This mechanism can explain why we identified higher Al^{3+} and Mn^{2+} content in solution where fire severity was lower.

On the other hand, plot topography can play an important role in fire behaviour. When the fire spread up a hill (as we observed in this study) the fuels are preheated prior the combustion. The fire spreads faster, and the temperatures reached are higher, producing also higher severities, depending on the amount part and type of vegetation combusted (Viegas 2004; Linn *et al.* 2007; Maingi and Henry 2007). This interaction between fire, topography and the increasing temperatures in their evolution, can explain the decreasing trend upslope in Fe^{2+} and Zn^{2+}.

The fire induced a higher variability in Fe^{2+} and Zn^{2+} spatial distribution in comparison with Al^{3+} and $Mn^{2+.}$ This means that plot topography can induce a bigger heterogeneity in HM distribution than burned species. The effect of terrain characteristics in burned severity and higher variability of nutrients released were also pointed out by Lorca and Ubeda (2004).

We observed different spatial distribution of HM released across the plot. These responses are consequence of the temperature reached and the burned specie. Studies elaborated by Pereira *et al.* (2008b), showed that $Al^{3+}$and Mn^{2+} have different responses of Fe^{2+} and Zn^{2+}, to fire temperatures. The first elements are released in substantial amounts at reduced fire temperatures – especially Al^{3+} from *Quercus suber* ash and Mn^{2+} from *Pinus* ash – that could occur in some parts of this plot. On the contrary, the impact of fire temperatures in Fe^{2+} and Zn^{2+} released from ash is a reduction in their concentration in solution in both species. This can explain why the studied HM has different behaviours, in their distribution and trends across the plot.

The solubility of $Al^{3+}$and Mn^{2+} are related with the burned specie and Fe^{2+} and Zn^{2+} with the evolution of fire temperatures across the plot. In these last HM, the effects of rising temperatures reduces their content in solution (Pereira *et al.* 2008b).

Future problems may occur when ash pH decreases, with leaching of macroelements over time. These HM before inhibited of solubilisation, will become more mobile, can rise in soil solution and became more available to plants, but also provoke a higher soil toxicity and environment degradation.

4. Conclusions

1. The ashes produced in this wildfire released more Al^{3+} and less Zn^{2+}.The major spatial variation was observed in Fe^{2+} and Zn^{2+} and this means that the variability of these elements across the plot is higher.

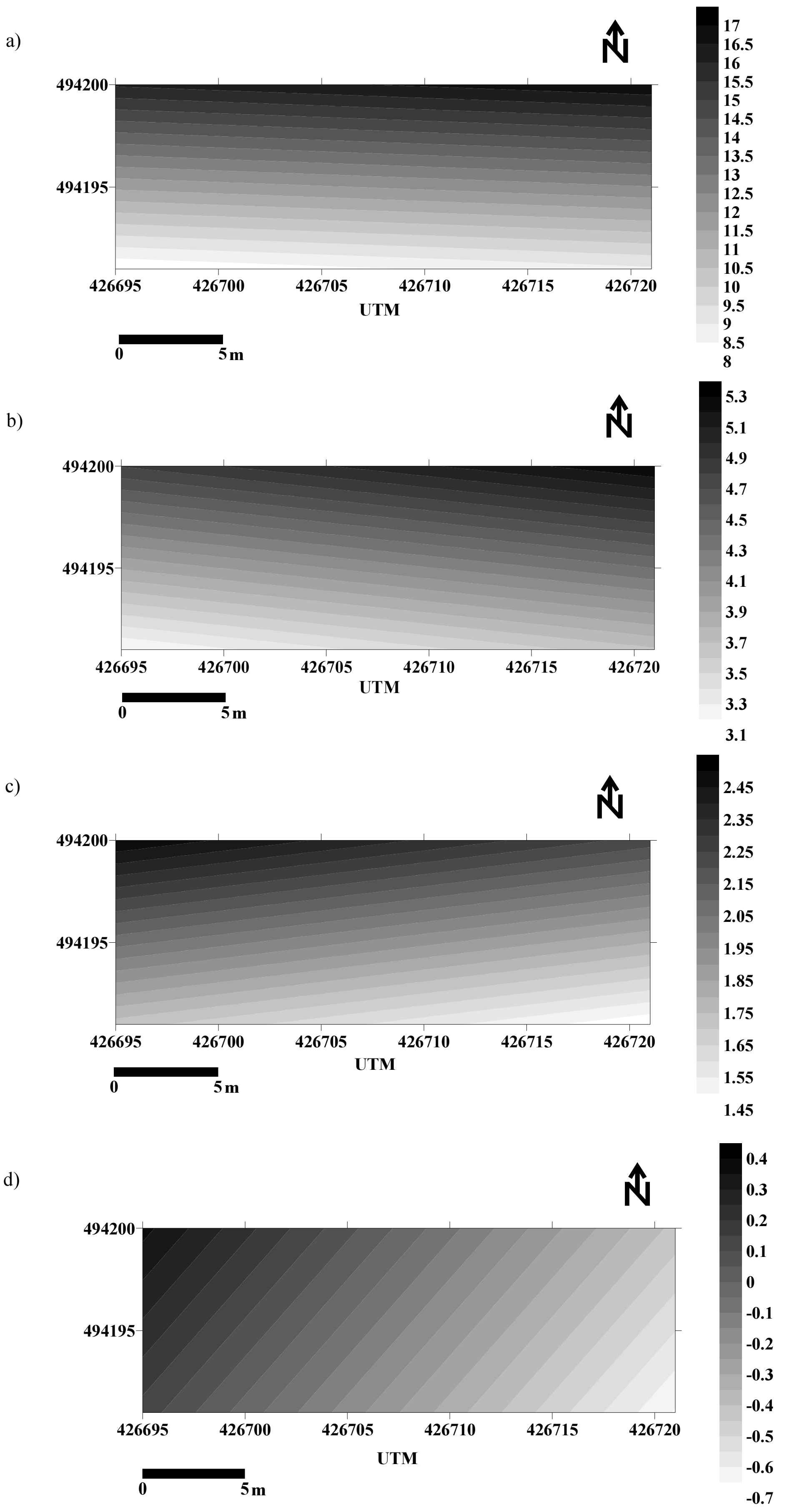

Fig. 4. Interpolated maps using PR method: a) Al^{3+}, b) Mn^{2+}, c) $Ln(Fe^{2+})$ and d) $Ln(Zn^{2+})$

2. When comparing with the other interpolation methods, the results of this work indicate that PR was the method most likely to produce the best estimation of all variables across the plot. This method allowed us to observe spatial distribution and trends of HM. In contrary, NN, presented in all HM tested the larger differences between observed and estimated (with exception of Ln(Fe^{2+})).

3. The amount of $Al^{3+}$and Mn^{2+} released from the ash, is related with the species distribution across the plot and burning severity. Fe^{2+} and Zn^{2+} concentrations in solution depend on other biophysical features as plot topography.

4. Fire spread upslope and consequent rising temperatures, induce a higher spatial variability in HM, than burned specie severity.

5. Further research is recommended and need evaluate the effect of fire in HM dynamic over the time and test other geostatistical methods in the evaluation of HM spatial distribution released from ash.

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PO GAISRO IŠ PELENŲ IŠSISKIRIANČIŲ SUNKIŲJŲ METALŲ ERDVINIS PASISKIRSTYMAS

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Santrauka

Didelės sunkiųjų metalų (SM) koncentracijos dirvožemyje ir vandenyje gali sukelti pavojų aplinkai ir žmogaus sveikatai. Pelenuose aptinkamos didelės SM koncentracijos, kurios priklauso nuo sudegusio medžio rūšies, tipo, sudegusios medžio dalies ir dirvožemio savybių. Po gaisro iš pelenų pasišalinantys SM patenka į dirvožemio tirpalą ir gali sukelti vandens išteklių taršą. SM išsiskyrimas iš pelenų teritorijos plote gali kisti. Darbe taikant interpoliacinius metodus tiriama SM – aliuminio (Al^{3+}), mangano (Mn^{2+}), geležies (Fe^{2+}) ir cinko (Zn^{2+}) – pasiskirstymas teritorijoje po *Quercus suber* ir *Pinus pinaster* miško gaisro Portugalijoje. Iš rezultatų matyti, kad nagrinėjamoje teritorijoje vidutiniškai didžiausios koncentracijos pasiskirstė Al^{3+}, o mažiausios – Zn^{2+}. Didžiausi koncentracijų pokyčiai buvo būdingi Zn^{2+} ir Fe^{2+}. Iš taikytų interpoliacinių metodų, prognozuojant SM pasiskirstymą teritorijoje, tikslesnis buvo polinominės regresijos metodas. Al^{3+} ir Mn^{2+} koncentracijų padidėjimas nustatytas iš pietinės teritorijos dalies šiaurinės link, o Fe^{2+} ir Zn^{2+} – sumažėjimas iš šiaurės vakarų dalies pietrytinės teritorijos dalies link. Al^{3+} ir Mn^{2+} išsiskyrimas iš pelenų priklausė nuo gaisro intensyvumo, o Fe^{2+} ir Zn^{2+} – nuo teritorijos topografijos. Gaisro intensyvumo pokyčiai teritorijoje ir su tuo susijęs temperatūros kilimas gali turėti didesnės įtakos SM pasiskirstymui teritorijoje negu sudegusių medžių rūšys. Laikui bėgant ir kintant pelenų pH, SM tampa judresni, tad gali patekti į dirvožemio tirpalą, sukelti pavojų aplinkai.

Reikšminiai žodžiai: sunkieji metalai, pelenai, *Quercus suber*, *Pinus pinaster*, erdvinė variacija, interpoliacijos metodai.

РАСПРЕДЕЛЕНИЕ В ПРОСТРАНСТВЕ ТЯЖЕЛЫХ МЕТАЛЛОВ, ВЫДЕЛЯЕМЫХ ПОСЛЕ ПОЖАРА ИЗ ЗОЛЫ

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Резюме

Большие концентрации тяжелых металлов (ТМ) в почве и воде могут быть опасны для окружающей среды и здоровья людей. Большие концентрации ТМ, выделяемые после пожара из золы, зависят от вида, типа, части сгоревшего дерева и свойств почвы. ТМ попадают в почву и могут вызвать загрязнение подземных вод. Выделение ТМ из золы на площади территории может меняться. В статье рассматривалось распределение после пожара на территории в Португалии таких тяжелых металлов, как алюминий (Al^{3+}), марганец (Mn^{2+}), железо

(Fe^{2+}) ir цинк (Zn^{2+}). С этой целью применялись методы интерполяции. Из результатов анализа видно, что на исследуемой территории в среднем наибольшими были концентрации Al^{3+}, а наименьшими Zn^{2+}. Наибольшим изменениям подвергались концентрации Zn^{2+} и Fe^{2+}. Из применявшихся методов интерполяции метод полиноминальной регрессии был наиболее точным для прогноза распределения ТМ на территории. Для Al^{3+} и Mn^{2+} было характерно увеличение концентраций с южной территории в сторону северной части, а для Fe^{2+} ir Zn^{2+} – уменьшение концентраций с северо-западной части в сторону юго-восточной территории. Выделение Al^{3+} и Mn^{2+} из золы после пожара зависело от интенсивности пожара, а в случае с Fe^{2+} и Zn^{2+} – от топографии территории. Изменение интенсивности пожара на территории и в связи с этим изменение температуры может оказывать бóльшее влияние на распределение ТМ на территории, чем вид сгоревших деревьев. С течением времени и изменением pH золы ТМ становятся более подвижными, могут попадать в подземные воды и тем самым создавать угрозу для окружающей среды.

Ключевые слова: тяжелые металлы, зола, *Quercus suber*, *Pinus pinaster*, пространственная вариация, методы интерполяции.

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