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# Main atmospheric heavy metal sources in Portugal by biomonitor analysis

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## Abstract

During the months of July and August of 1993 a lichen collection campaign was held in Portugal where about 250 samples were collected and analysed by thick target PIXE and INAA. Results for 43 different elements were obtained and a data base was built and subjected to Monte Carlo aided target transform factor analysis (MCATTF), method developed at IRI TU Delft.  $10 \times 10$  km coast and  $50 \times 50$  km far from coast sampling grids were used for collection, concentration data as well as factor patterns were extrapolated to the whole country making use of an extinction rule of  $1/r^3$ . In this work we present the results that were obtained based on a reduced data set of 22 elements measured by TTPIXE. The results for INAA data subset and the total data set are presented elsewhere.

## 1. Introduction

Exhaustive studies about total element deposition in Portugal have never been done. Following the procedure already applied in The Netherlands [1] lichens *Parmelia Sulcata* were collected from Olive Trees all over Portugal. In this work we applied Monte Carlo aided target transform factor analysis to the data obtained by PIXE analysis. It was possible to identify 9 factors, 4 of which were associated with natural sources. Smelters, traffic combined with phosphate products, agricultural activity (including wire production) and cement production were the anthropogenic sources better identified. One factor could not be well understood although it is geographically well delimited.

## 2. Experimental procedure

Two collecting grids were defined in order to better study the most industrialised region. Near the coast lichens were collected on a  $10 \times 10$  km grid. Towards the interior of the country, as no special industry exists, a  $50 \times 50$  km grid was used. Lichens were collected in a total of 228 different locations. In 10% of the places five samples were picked in order to be able to establish local variations. In addition to samples, one IAEA 336 Lichen reference material [2], and one CTA-OTL-1 certified reference

material from the Polish ICHTJ<sup>®</sup>, were analysed for every 50 samples batch, in order to assure quality control. A total of 350 targets were analysed by TTPIXE for which radiation damage corrections were considered (see other communication in this conference).

Spectra obtained with a 200 eV Ortec Si(Li) X-ray detector were analysed with AXIL computer code [3] and concentrations were then calculated with DATTPIXE [4]. Hand typing was reduced to the minimum to prevent typing mistakes. A special code was developed to convert results from DATTPIXE output format to TUDelft FA program format. Data were still checked for statistically strange results and one defective result found was excluded.

Data were then analysed by Monte Carlo target transform factor analysis [5]. The number of factors was chosen as 9 by applying the assignment conflict method [6]. The assignment conflict graphic is presented in Fig. 1.

## 3. Results and discussion

The 9 factors composition are presented in Table 1 in weight percentage. For each factor, the correlation bases composition is converted to the original bases by multiplying with the standard deviation for each element. Afterwards, each factor is normalised to 100% considering all elements. Nevertheless, as one of the parameters of this MCATTF procedure is the probability of a given element having null concentration in a factor, only the elements for which this probability is less than 32% are considered.

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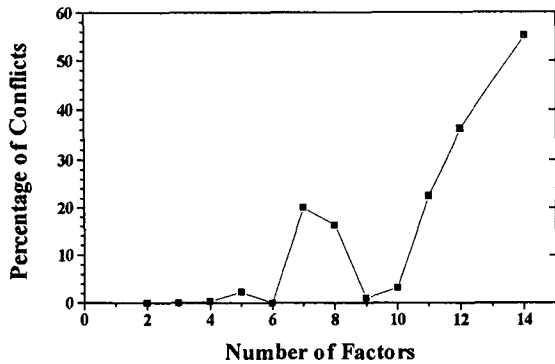


Fig. 1. Assignment conflict graph.

This choice was taken in order to make use of as much significant values as possible during interpretation.

The average contribution of each factor for the measured variations of each element can be seen in Table 3.

In Fig. 2 we present the factor values patterns. These were obtained from the factor values for the sampling places by extrapolation based in a  $1/r^3$  extinction rule. This means that the weight of any node of the sampling net to any other point in the map is proportional to the third power of inverse of the distance. This is chosen to prevent against the use of artificially defined cut-off distances.

For interpretation, the total global emissions for several types of sources presented by Nriago [7] were assumed as

representing mean composition for the emission of the respective type of sources. These were then compared to the 9 factors obtained by calculating the cosines of the angle between the N-dimensional concentration space vectors of factors and of Nriago's sources. For that, a sub-space of the common elements: V, Cr, Mn, Ni, Cu, Zn, As and Pb was considered. The values obtained are presented in Table 2. To get a better insight on the meaning that could be extracted from this comparison, the same procedure was applied to Nriago's mean sources themselves, in this case considering every element present in his data.

The results showed some correlation within natural sources, and also within anthropogenic sources. The cross-correlation between natural and anthropogenic is nevertheless reduced to incineration and secondary non-ferrous metals purification activities.

From Table 2 we can identify four natural sources: factors 1, 4, 7 and 8; and four anthropogenic sources: factors 2, 3, 5 and 6. As for factor 9 the faint correlation to seasalt aerosol cannot be straightforwardly interpreted as the major elements were not considered and chlorine is not even slightly correlated to this factor. Also factor 5 can conjugate both natural and anthropogenic sources.

Factors 1, 7 and 8 can be further interpreted through the Fe/Si concentration ratios, as limestone, basalt and shale. Factor 1, nevertheless shows no concentration on Ca, so eliminating the straightforward interpretation as limestone. Comparing the factor values pattern to Portuguese

Table 1

Factor composition in wt.%. Although normalization to 100% includes all elements, only the values for which there is 68% confidence of the occurrence of the element in the factor are presented. The letter P identifies the pilot element of the factor which means that it presents the highest correlation with the factor

| Elem | F1     | F2    | F3    | F4    | F5    | F6    | F7     | F8     | F9     |
|------|--------|-------|-------|-------|-------|-------|--------|--------|--------|
| Si   | 78     | 44    | 14    | 13    | 33    | 3.7   | 63     | 62     | 62     |
| P    |        |       | 21    |       | 17    |       | 1.4    | 3.5    |        |
| S    |        | 9.1   | 38 P  |       | 3.6   | 1.1   |        | 0.61   | 9.6    |
| Cl   |        |       |       | 78 P  |       |       | 0.9    | 0.66   |        |
| K    | 7      | 9.6   | 21    |       | 38 P  |       | 5.8    | 17     | 4.1    |
| Ca   |        |       |       |       |       | 93 P  |        |        |        |
| Ti   | 1.7    | 3.3   | 0.77  |       |       | 0.25  | 2.3    | 1.6    | 2.2    |
| V    | 0.01   | 0.8   | 0.063 | 0.24  |       |       | 0.11   |        | 0.86   |
| Cr   |        |       | 0.011 | 0.048 |       |       | 0.17 P |        |        |
| Mn   | 0.14   | 0.15  |       |       | 0.39  |       | 0.52   | 0.38   |        |
| Fe   | 12     | 28    | 2.7   |       | 4.9   | 0.92  | 25     | 13     | 18     |
| Ni   |        | 0.17  |       | 0.034 |       |       | 0.044  | 0.003  | 0.21 P |
| Cu   |        |       |       | 0.9   | 1.0   |       |        |        | 1.6    |
| Zn   |        | 2.2   | 0.8   |       | 1.9   | 0.14  | 0.24   | 0.09   | 1.2    |
| Ga   | 0.008  | 0.017 |       |       | 0.014 | 0.001 | 0.008  | 0.005  | 0.005  |
| As   | 0.014  | 0.23  |       | 0.11  | 0.045 |       | 0.023  |        | 0.022  |
| Br   | 0.026  |       | 0.5   | 1.0   |       |       |        |        | 0.053  |
| Rb   | 0.091  |       |       | 0.087 | 0.34  |       |        | 0.095  |        |
| Sr   | 0.020  | 0.048 |       | 0.055 |       | 0.009 |        | 0.51 P |        |
| Zr   | 0.16 P |       | 0.039 | 0.19  |       | 0.020 |        | 0.020  | 0.13   |
| Ba   | 0.12   |       |       |       |       | 0.007 |        | 0.55   | 0.067  |
| Pb   | 0.04   | 1.5 P | 0.32  | 0.13  | 0.16  | 0.054 | 0.086  | 0.051  |        |

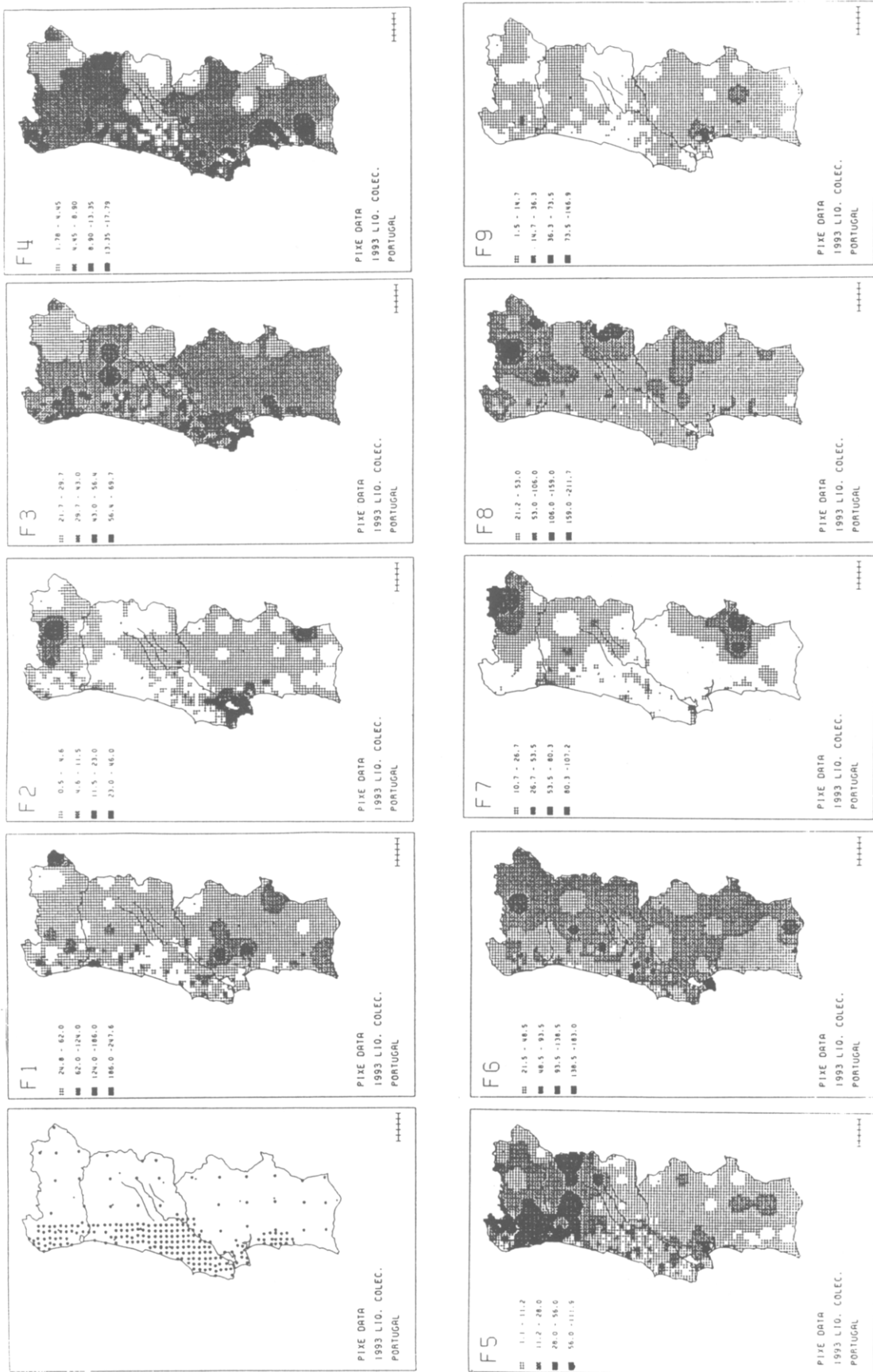


Fig. 2. Factor values patterns. The factor values obtained for each sampling point are extrapolated to all points in the map by using a  $1/r^3$  extinction rule.

Table 2

Cos (N-dimensional vector angles) between Lichens Factors and Nriago 89 mean sources, only values greater than 0.75 are presented. WIND – windblown dust; SEAS – seasalt spray; VOLC – volcanoes; FIRE – wild forest fires; BIO – biogenic (P – continental particles, V – continental volatiles, M – marine); COAL – coal combustion; OILE – oil combustion; NFNM – non-ferrous metals mine operation; PBPR – lead production; CUNI – Cu/Ni production; ZNPR – zinc production; SECN – secondary non-ferrous metals; IRON – iron and steel manufacture; INCE – refuse incineration; FOSF – phosphate fertilizers; CEME – cement production; FUEL – fuel wood combustion

|      | Fac1 | Fac2 | Fac3 | Fac4 | Fac5 | Fac6 | Fac7 | Fac8 | Fac9 |
|------|------|------|------|------|------|------|------|------|------|
| WIND | 0.95 |      |      |      |      |      | 0.92 | 0.96 |      |
| SEAS |      |      |      | 0.85 |      |      |      |      | 0.77 |
| VOLC | 0.85 |      |      |      |      |      | 0.93 | 0.88 |      |
| FIRE | 0.91 |      |      |      |      |      | 0.93 | 0.98 |      |
| BIOP |      |      |      | 0.94 |      |      |      |      |      |
| BIOV |      |      | 0.77 |      | 0.83 | 0.77 |      |      |      |
| BIOM |      |      |      |      | 0.76 |      |      |      |      |
| COAL |      |      |      |      |      |      | 0.76 |      |      |
| OILE |      |      |      |      |      |      |      |      |      |
| NFMM |      |      |      |      |      |      |      |      |      |
| PBPR |      |      |      |      |      |      |      |      |      |
| CUNI |      |      |      | 0.79 |      |      |      |      |      |
| ZNPR |      | 0.85 | 0.97 |      | 0.88 | 0.97 |      |      |      |
| SECN | 0.97 |      |      |      |      |      | 0.87 | 0.98 |      |
| IRON |      | 0.75 | 0.80 |      |      | 0.79 |      |      |      |
| INCE | 0.81 |      |      |      |      |      | 0.95 | 0.90 |      |
| FOSF |      | 0.80 | 0.93 |      | 0.91 | 0.94 |      |      |      |
| CEME |      | 0.95 | 0.96 |      |      | 0.96 |      |      |      |
| FUEL |      | 0.91 | 0.93 |      | 0.83 | 0.93 |      |      |      |

Geological Soil chart, this can be identified as recent sediment soil (mesozoic, cenozoic and anthropozoic deposits), the lack of Ca in the factor remains nevertheless an interesting fact. Factors 7 and 8 based on this approach are identified as eruptive rocks, and old metamorphic based soil (precambrian and palaeozoic soils), totally compatible with the previous Fe/Si ratio based interpretation.

Factor 4 is highly correlated to biogenic particles and seasalt spray, a high concentration in chlorine confirms that interpretation. The correlation to Cu/Ni production from Table 2 is originated from an intrinsic correlation that can be found also within Nriago's data.

Factors 2, 3 and 6 are very similar by comparison with Nriago's data. The content in sulphur is nevertheless quite different. For factor 2 the low contents in sulphur and high contents in iron and zinc should indicate smelters and zinc production as responsible for this factor. The high correlation to cement production cannot be further considered due to the total lack of calcium in this factor. Factor 3, in opposition to factor 2, presents high contents in sulphur, phosphorous and potassium but low content in iron. The high correlation with zinc production should be carefully considered as phosphate fertilisers and zinc production appear highly correlated within Nriago's data. The high value of sulphur as well as the ratio of Br/Pb of 1.6 take us to attribute this factor also to traffic, both diesel and gasoline, even because Br in lichens material tends to be slightly underestimated by TPIXE [2]. We so interpret this factor as combined production and use of phosphate products and traffic.

Finally in this group there is factor 6, the strong connection of calcium immediately associates this factor to cement production. The comparison of the factor values maxima positions and the Portuguese Cement Production Plants locations reveals a quite good site to site identification.

For a complete interpretation only factors 5 and 9 are missing.

Factor 5 resembles a soil factor. Its high content in phosphorous and potassium, as well as the presence of sulphur and copper and zinc, take us to consider this factor as due to resuspension of particles originated from agricultural soils and cultures. Also its geographic distribution is correlated to areas of commercial wine production. The only slight drawback in this interpretation is the lack of presence of Ca in this factor as the traditional method for vineyard treatment includes calcium hydroxide in its composition, side by side with copper and zinc sulphides. Nevertheless, some conflicts to factor 3 also corroborate this interpretation.

Finally factor 9 is only correlated to seasalt spray, in Table 3, missing the correlation to Cu/Ni production (present in Nriago's data). The total lack of chlorine in the factor takes us to assume that this correlation is purely occasional so it was not pursued any further. Although no special correlation could be found connecting this factor to oil combustion, the V/Ni ratio is quite compatible with this interpretation. The Fe/S ratio also resembles the Fe/S ratio that can be found in pyrite. We so interpret this factor as due to resuspension of pyrite material from a recently

Table 3

Average % contribution to total elemental occurrence. Only the values for elements of which there is less than 32% of probability of null concentration in the factor are presented

| Elem | F1 | F2  | F3 | F4   | F5  | F6  | F7   | F8  | F9  |
|------|----|-----|----|------|-----|-----|------|-----|-----|
| Si   | 36 | 1   | 6  | 1    | 5   | 2   | 6.5  | 31  | 3   |
| P    |    |     | 59 |      | 18  |     | 1    |     |     |
| S    |    | 1   | 70 |      | 2.5 | 2.7 |      | 1   | 2   |
| Cl   |    |     |    | 50   |     |     | 1    | 3   |     |
| K    | 6  | 10  | 18 |      | 12  |     | 1.1  | 16  | 0.4 |
| Ca   |    |     |    |      |     | 80  |      |     |     |
| Ti   | 30 | 3   | 12 |      |     | 5.7 | 8.8  | 31  | 4   |
| V    | 3  | 11  | 16 | 11   |     |     |      | 1.4 | 25  |
| Cr   |    |     | 20 | 15   |     |     | 72   |     |     |
| Mn   | 15 | 1   |    |      | 14  |     | 12.1 | 44  |     |
| Fe   | 26 | 3   | 5  |      | 3.7 | 2.6 | 12.3 | 31  | 4   |
| Ni   |    | 9   |    | 6    |     |     | 10.1 | 4   | 22  |
| Cu   |    |     |    |      | 46  |     |      |     | 23  |
| Zn   |    | 7   | 43 |      | 37  | 10  | 3    | 6   | 7   |
| Ga   | 31 | 4   |    |      | 19  | 5   | 7.4  | 19  | 2   |
| As   | 14 | 13  |    | 18.7 | 15  |     | 5.4  |     | 2.5 |
| Br   |    |     | 84 | 30.6 |     |     |      |     | 1   |
| Rb   | 21 |     |    |      | 28  |     |      | 24  |     |
| Sr   | 4  | 0.5 |    | 1.7  |     | 2   |      | 105 |     |
| Zr   | 50 |     | 11 | 9.33 |     | 8   |      | 6   | 4   |
| Ba   | 25 |     |    |      |     | 1.4 |      | 104 | 1.5 |
| Pb   | 9  | 17  | 66 | 5    | 12  | 15  | 4    | 12  |     |

unoperative pyrite mining load terminal. This interpretation can be further supported by the slight maxima that can be found in a region of also recently unoperative pyrite mining. The V/Ni ratio correlation could, under this interpretation be understood by the resuspension of deposited material originated from a nearby oil based energy production unit, and also the correlation to seasalt spray would be based on resuspension of this type of material as the maxima are close to sea.

#### 4. Conclusions

A resume of factor assignments is presented in Table 4. It is also verified that the factor values maxima do coincide quite well with the sites where maxima should be expected for each of them. In some cases geographic distribution was used for interpretation but, when this is not the case, as factor 6, the reproduction of expected maxima is very good.

The contribution of natural sources to deposition measured in this way is important for some elements like Ti, Cr, Mn, Fe and As.

Table 4

Factor assignment

|          |   |
|----------|---|
| Factor 1 | Recent sedimental soil                                      |
| Factor 2 | Smelters  |
| Factor 3 | Diesel and gasoline based traffic and phosphated products   |
| Factor 4 | Seasalt spray and biogenic particles                        |
| Factor 5 | Agricultural activities including wine production           |
| Factor 6 | Cement production   |
| Factor 7 | Eruptive rocks based soil                                   |
| Factor 8 | Shale and old soils from metamorphic rocks                  |
| Factor 9 | Resuspension of material from pyrite manipulation processes |

Traffic and associated sources in factor 3 represent a very important pollution source of many elements as P, S, V, Cr, Zn, Br and Pb.

Smelters contribute significant to V, As and Pb deposition.

#### Acknowledgements

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