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Bio-monitoring of trace-element air pollution in Portugal: Qualitative survey

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During the months of July and August 1993 a lichen collection campaign was held in Portugal where about 250 samples were collected and analysed by thick target TTPIXE and INAA. Results for 44 different elements were obtained and a data base was built and subjected to Monte Carlo Aided Target Transform Factor Analysis (MCATTFA), a method developed at IRI (Delft). 10×10 km^2 coast and 50×50 km^2 far from coast sampling grids were used for collection. In this work we will present the results which were obtained based on a reduced data set of 36 elements measured by INAA. The results for 22 elements obtained by TTPIXE were published elsewhere. In this work we will also present the conclusions considering all the 44 elements determined by both techniques.

Introduction

The use of plants for air pollution studies is increasing in the last years. Exhaustive studies concerning total element deposition in Portugal has never been done. Following the procedure already applied in The Netherlands[1] lichens *Parmelia sulcata* were collected from olive trees all over Portugal. Two sampling grids were defined in order to better study the most industrialised region. Near the coast lichens were collected on a 10×10 km^2 grid. Towards the interior of the country, as no special industry exists, a 50×50 km^2 grid was used. In this work we applied Monte Carlo Aided Target Transform Factor Analysis to the data obtained by INAA analysis, following the same procedure used previously[2] with data obtained by PIXE. We discuss the pollution source identification using the INAA set and the (INAA + PIXE) data.

Experimental

Sample of *Parmelia sulcata* were collected from olive tree substrate, at 1-2 m from the soil, in a total of 228 different locations, in July and August 1993. Each sample was a mixture of 5 sub-samples taken from 5 different olive trees; in 10% of the places the 5 samples were analysed separately to determine local variations.

The substrate was carefully removed, the lichens were put on nylon sieves and washed for 30 seconds, freeze-dried and ground in Teflon capsules. Pellets of 500 mg were made for long irradiation (5 h); 50 mg up to 200 mg were used in short irradiation (30 s). The long irradiations were done in the Portuguese Research Reactor, and the short irradiations in the reactors of the Interfaculty Reactor Institute (Delft) and Hahn-Meitner Institut (Berlin). The samples were measured in HPGe detectors (FWHM ~ 1.85 keV at 1.33 MeV), after 4 days and 4 weeks (long irradiation) and after 10 minutes (short irradiation). Gold and zinc were used as comparators in k_0-method[3] for long and short irradiations, respectively. The relative method was used in the Hahn-Meitner Institut. Similar methodology was applied to the reference materials NIST Tomato Leaves, Pine Needles, and Citrus Leaves, and IAEA 336 lichen,[4] used in the quality control.

Hand typing of the data was reduced to the minimum to prevent for typing mistakes. A special code was developed to convert results from HPGECONC[5] output format to TUDelft Factor Analysis format. Data were checked for statistically strange results and then analysed by Monte Carlo Aided Target Transform Factor Analysis.[6] By applying the assignment conflict method[7] the number of factors was chosen as 10 for the INAA set. Putting together the INAA and the PIXE data a global data set was created for which the number of factors was chosen as 11 by applying the same method.

Results and discussion

Figure 1 shows the ratio (INAA/certified value) for the reference materials refered above and analysed for quality control of the analysis of *Parmelia sulcata*. No systematic errors are evident in the figure. It is observed that ~ 68% of the values are in the interval 0.9–1.1, the uncertainty being estimated in ± 10%.

In a previous work[2] data obtained by PIXE analysis and the corresponding factors were presented. In Tables 1 and 3 we present the composition profiles obtained for the principal pollution sources, by applying MCATTFA[6] to INAA data for the same sample set, and to the conjugation of both techniques' data. As a first result we verified an increase in the number of factors both from PIXE to INAA and from INAA to the global data set. Restricted to PIXE results 9 factors were found,[2] INAA data provides us with 10 factors and finally the full data set solves the problem by considering 11 factors. The good number of factors was obtained in all cases by the conflict assignment method.[7] The increase in the number of factors is supported by the

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Table 1. Factors composition in wt% for factors obtained using INAA data only. Although normalisation to 100% includes all elements, only those for which there is 95% confidence of 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

Element	Fac 1	Fac 2	Fac 3	Fac 4	Fac 5	Fac 6	Fac 7	Fac 8	Fac 9	Fac 10
Na	2.753	3.820	2.157	15.75	1.508	6.090	4.872	1.552	2.507	8.816
Mg	9.734	8.605	12.87						14.56	12.78
Al	50.52	55.56	43.23						43.20	43.18
Cl			5.863	7.405	86.43 P					
K	9.812	20.71	23.29	31.55		32.34	52.85	5.545	13.32	
Ca								79.19 P		
Sc	0.0083 P	0.0017	0.0029	0.0074		0.0052	0.010	0.0021	0.0061	0.0065
Ti	3.196	1.338	1.275	3.000		2.404		0.660	2.742	
V	0.137				2.290	0.513				0.503
Cr	0.0420		0.0379			0.0510	0.0537	0.0378	0.0637	0.0932
Mn		0.206					0.393		2.070 P	
Fe	22.72	7.408	9.763	23.76		31.07	31.54	6.138	15.79	24.64
Co	0.0095		0.0024	0.0062	0.0012	0.0075	0.0122	0.0028	0.0067	0.0095
Ga	0.0204									0.0691
As		0.0050	0.144			0.0959		0.0090	0.0083	
Se	0.0014	$8.9 \cdot 10^{-4}$	0.0025	0.0072		0.0033.	0.037	$4.7 \cdot 10^{-4}$		
Br				0.767 P						
Rb		0.193 P	0.115				0.149			0.0878
Sr							0.815 P			
Sb			0.0022			0.0611 P				0.0119
I										0.569 P
Cs	0.0039	0.0096	0.0044	0.0037	0.0027		0.0096	0.0015	0.0023	0.0054
Ba	0.256	0.183	0.0695		0.0981	0.439	0.920		0.143	
La	0.0279	0.0276	0.0199	0.0433		0.0242	0.0517	0.0078		
Ce	0.0591	0.0603	0.0377	0.0631		0.0575	0.113	0.0129		
Nd	0.0316	0.0301			0.0332	0.0979	0.0431		0.0330	
Sm	0.0039	0.0035	0.0030			0.0020	0.0052	0.0010	$8.4 \cdot 10^{-4}$	
Eu	0.0019	$7.6 \cdot 10^{-4}$	$7.9 \cdot 10^{-4}$	0.0023		0.0020	0.0031	$5.5 \cdot 10^{-4}$	$6.8 \cdot 10^{-4}$	$7.2 \cdot 10^{-4}$
Tb	$6.5 \cdot 10^{-4}$	$3.6 \cdot 10^{-4}$	$2.7 \cdot 10^{-4}$	$6.5 \cdot 10^{-4}$		$6.1 \cdot 10^{-4}$	$9.9 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$	$2.1 \cdot 10^{-4}$	$3.2 \cdot 10^{-4}$
Lu	$3.3 \cdot 10^{-4}$	$1.1 \cdot 10^{-4}$	$0.8 \cdot 10^{-4}$	$3.5 \cdot 10^{-4}$		$2.8 \cdot 10^{-4}$	$4.0 \cdot 10^{-4}$	$0.7 \cdot 10^{-4}$		
Hf	0.0046	0.0035	0.0017	0.0061		0.0052	0.0055	0.0012		
Ta	$6.0 \cdot 10^{-4}$	$8.3 \cdot 10^{-4}$	$4.3 \cdot 10^{-4}$	0.0011		$4.7 \cdot 10^{-4}$	$9.8 \cdot 10^{-4}$	$2.7 \cdot 10^{-4}$	$1.9 \cdot 10^{-4}$	
W			0.0761 P		0.0079					
Hg				0.0054	$7.5 \cdot 10^{-4}$	0.0139			0.0026	
Th	0.0081	0.0161	0.0067	0.0086		0.0089	0.0127	0.0013		
U		0.0047	0.0050	0.0034					0.0030	

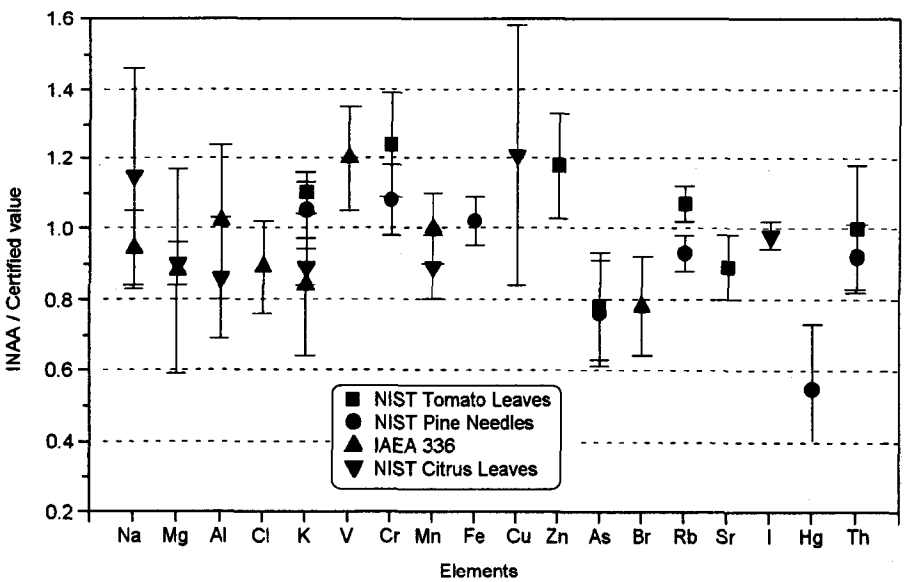

Fig. 1. Ratio INAA/certified values for quality control of INAA analysis

Table 2. Cos(N-dimensional vector angles) between Lichens Factors and Nriago 89 mean sources for factors obtained using only INAA data. 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 – Phosfate fertilizers; CEME – Cement production; Fuel – Fuel wood Combustion; VARI – Various Mobile Sources

	Fac 1	Fac 2	Fac 3	Fac 4	Fac 5	Fac 6	Fac 7	Fac 8	Fac 9	Fac 10
WIND		0.98					0.99		0.98	
SEAS	0.84				0.82	0.91				0.84
VOLC		0.93					0.97		0.94	
FIRE		1.00					0.99		1.00	
BIOP		1.00					0.99		1.00	
BIOV										
BIOM										
COAL										
OILE	0.96				1.00	0.97				0.99
NFMM		0.97					0.96		0.97	
PBPR			0.92							
CUNI			0.94							
ZNPR			0.91							
SECN		1.00					0.99		1.00	
IRON								0.99		
INCE		0.97					0.97		0.97	
FOSF										
CEME								0.99		
FUEL										
VARI			0.97							

increase in the number of elements used: 22 for PIXE data, 36 for INAA data, and 44 for the global data set. It should be emphasised that the increase by a factor of 2 in the number of different elements considered produced two additional factors and a redefinition of the composition of factors.

For the interpretation of the data we have followed a similar procedure as explained in the previous work.[2] This procedure is here explained again for completness.

For each factor, the correlation basis factor profile is converted to the original bases multiplying by the standard deviation for each element. Afterwards, each factor is normalised to 100% considering all elements. Nevertheless, as one of the parameters of this MCATTFA procedure is the probability of a given element having zero concentration in a factor, only the elements for which this probability is less than 5% are considered. This restriction can be used in this work because the factors are better defined; this is due to the larger number of elements determined as compared to the PIXE data.

Based on these factors composition we calculated their correlation to NRIAGO's[8] mean sources by calculating the cosines of the angle between the N-dimensional vectors representing each factor and/or mean source in an element concentration space. For these calculations only the elements V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sb, Hg, and Pb were used as these were the only common elements to NRIAGO's table and our results. The results obtained for the INAA data and for the global data set are presented in Tables 2 and 4, respectively. The same procedure was carried out for the auto-correlation matrix for the global data set factors, and for the correlation between each of the data sets taken individually and the global data set. Through the analysis of the global data set autocorrelation matrix we verified that factors 1 to 5 and factor 9 are greatly correlated to each other.

In the following we shall deal with the interpretation of the factors obtained from the global data set. In the text that follows, the factors in discussion will be the global factors presented in Table 3 unless stated otherwise. In Figs 2, 3 and 4 the factor values patterns are presented. In Table 5 it is shown the average contribution of each factor for the measured variation of each element. This is equivalent to the contribution of the factor to the occurrence of the element. In Table 6 a resumé of the factor assignments is presented.

From Table 4 we can see that factor 1 (INAA factor 2 in Table 1) can be assigned to natural soil source. From its Fe/Si ratio we can further say it is shale based soil. This factor is well correlated to the whole lanthanide series which is a typical behavior of a soil contribution. In spite of the strange Al/Si ratio we still believe this factor is soil contribution. This factor is responsible for 20% of the Al, 28% for Th and 26% for U. Also the lanthanide series is justified 15–38% by this factor, as well as about 20% of Zr, Cs, Hf and Ta.

Factor 2 (INAA factor 10 in Table 1), although slightly correlated to oil combustion, has Ga as pilot element. Meanwhile INAA factor 10 has iodine as pilot element. From KABATA-PENDIAS[9] Ga and I are both connected to coal

Table 3. Factor composition in wt% for factors obtained using INAA and PIXE data. See also Table 1

Element	Fac 1	Fac 2	Fac 3	Fac 4	Fac 5	Fac 6	Fac 7	Fac 8	Fac 9	Fac 10	Fac 11
Na	2.274	1.871	1.919	0.906		1.823	4.824	13.780	3.757	4.810	
Mg	4.493	8.131	8.334	4.823	4.002				7.600		1.105
Al	32.45	28.83	35.73	15.48	18.94				22.81		
Si	42.80	34.20	15.33	62.21	50.88				30.90	32.62	8.658
P			7.454					8.662			1.385
S			3.266		9.976	3.159	19.54	21.91			1.743
Cl				4.090		79.96 P		7.069			
K	8.453		21.78	6.453		4.749	13.05	17.57	14.28	32.37	
Ca											81.71 P
Sc	0.0026	0.0066		0.0012				0.0018	0.0048	0.0076	$4.7 \cdot 10^{-4}$
Ti	0.924	1.530		1.482	1.557		2.285		0.700	1.104	0.418
V		0.202			0.485	2.083	0.572				
Cr	0.0069	0.0595		0.0162			0.0467		0.0442	0.0412	
Mn	0.1068					0.335			1.006 P		
Fe	7.973	18.61	4.149	3.537	5.953	1.980	22.07	9.632	11.99	22.61	1.164
Co	0.0023	0.0085		$8.2 \cdot 10^{-4}$	0.0037				0.0046	0.0085	0.0015
Ni		0.0469		0.070	0.127	0.0691	0.101				
Cu			0.306		1.256 P				0.407		
Zn		0.154	0.674		1.029	0.0736	1.438	0.379		0.479	0.139
Ga	0.0035	0.028 P									0.0036
As		0.0100	0.0202	0.0719			0.100			0.0096	
Se	$7.6 \cdot 10^{-4}$	$7.3 \cdot 10^{-4}$		0.0012			0.0028	0.0051		0.0033	
Br								0.591		0.260	
Rb	0.0723		0.162 P			0.0186					
Sr			0.0933			0.0583				0.402 P	
Zr	0.0878			0.154	0.184						0.0364
Sb		0.0020					0.0615 P				
I		0.0542						0.420 P			
Cs	0.0049	0.0016	0.0063	$9.6 \cdot 10^{-4}$		0.0042		0.0051		0.0035	
Ba	0.130	0.155	0.144			0.148	0.360			0.389	0.0326
La	0.0179	0.0121	0.0164	0.0073	0.0136		0.0156	0.0222		0.0355	
Ce	0.0402	0.0240	0.0338	0.0141	0.0244		0.0374	0.0206		0.0677	0.0028
Nd	0.0259 P	0.0125				0.0382	0.0862		0.0178	0.0178	
Sm	0.0024	0.0021	0.0020	0.0013	0.0014					0.0029	$3.2 \cdot 10^{-4}$
Eu	$8.4 \cdot 10^{-4}$	0.0011		$4.2 \cdot 10^{-4}$	$6.5 \cdot 10^{-4}$		$8.8 \cdot 10^{-4}$	$6.6 \cdot 10^{-4}$	$7.0 \cdot 10^{-4}$	0.0022	$1.9 \cdot 10^{-4}$
Tb	$3.2 \cdot 10^{-4}$	$3.9 \cdot 10^{-4}$	$1.4 \cdot 10^{-4}$	$1.2 \cdot 10^{-4}$	$1.8 \cdot 10^{-4}$		$2.9 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$	$2.2 \cdot 10^{-4}$	$6.7 \cdot 10^{-4}$	$0.40 \cdot 10^{-4}$
Lu	$1.4 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$		$0.61 \cdot 10^{-4}$	$1.3 \cdot 10^{-4}$				$1.1 \cdot 10^{-4}$	$3.2 \cdot 10^{-4}$	$0.20 \cdot 10^{-4}$
Hf	0.0029	0.0014	0.0010	0.0011	0.0031			0.0022		0.0043	$3.1 \cdot 10^{-4}$
Ta	$4.8 \cdot 10^{-4}$	$2.6 \cdot 10^{-4}$	$5.0 \cdot 10^{-4}$	$1.5 \cdot 10^{-4}$				$7.8 \cdot 10^{-4}$	$2.3 \cdot 10^{-4}$	$7.0 \cdot 10^{-4}$	
W	0.0016			0.0437 P		0.0060					0.0011
Hg					0.0021		0.0110	0.0019	0.0028	0.0020	
Pb	0.0253	0.0838	0.107	0.104	0.190		1.477				0.0776
Th	0.0083		0.0103		0.0048		0.0085	0.0065		0.0067	
U	0.0019		0.0038	0.0017				0.0031	0.0020	0.0012	

combustion. So this factor is probably due to coal combustion and a slight correlation to a factor identified as smelters in the previous work can justify the fact that we could not correlate this factor to NRIAGO's coal combustion. The factor values pattern (Fig. 2) nevertheless presents factor maxima which can not be understood by this interpretation, namely the big North, interior South and Southwest maxima. The North and South maxima would better indicate some connection to mining processes. This factor is responsible for 24% of the Ga and 10–15% of V, Cr, Fe, Co, Ni. It is interesting to note that the contribution to Pb is similar to factor 1 which is a natural source.

Factor 3 (INAA factors 2 and 3 in Table 1) can be interpreted as phosphate fertilisers, this factor can also be correlated to agricultural activities which will justify the high K, Cu and Zn levels. It has Rb as pilot element and it is correlated to a factor identified also as agriculture activities in the previous work. The corresponding INAA factor 3 has W as pilot element which is the pilot element of factor 4 in the global data set. This factor 4 (INAA factor 3) is also correlated to mobile sources as can be seen from Table 4. The factor values pattern is not compatible with this hypothesis. By comparing the maxima with the location of the biggest Portuguese industrial sources, a mixture of Electrical Power Plant and Paper Paste industry would arise for this factor. The complex correlation of this factors is still unclear also because of the higher correlation to NRIAGO's Pb production. Factor 3 contributes 31% for the Rb and similarly to Cu, Zn, As, Cs, Th, U (44%). It also

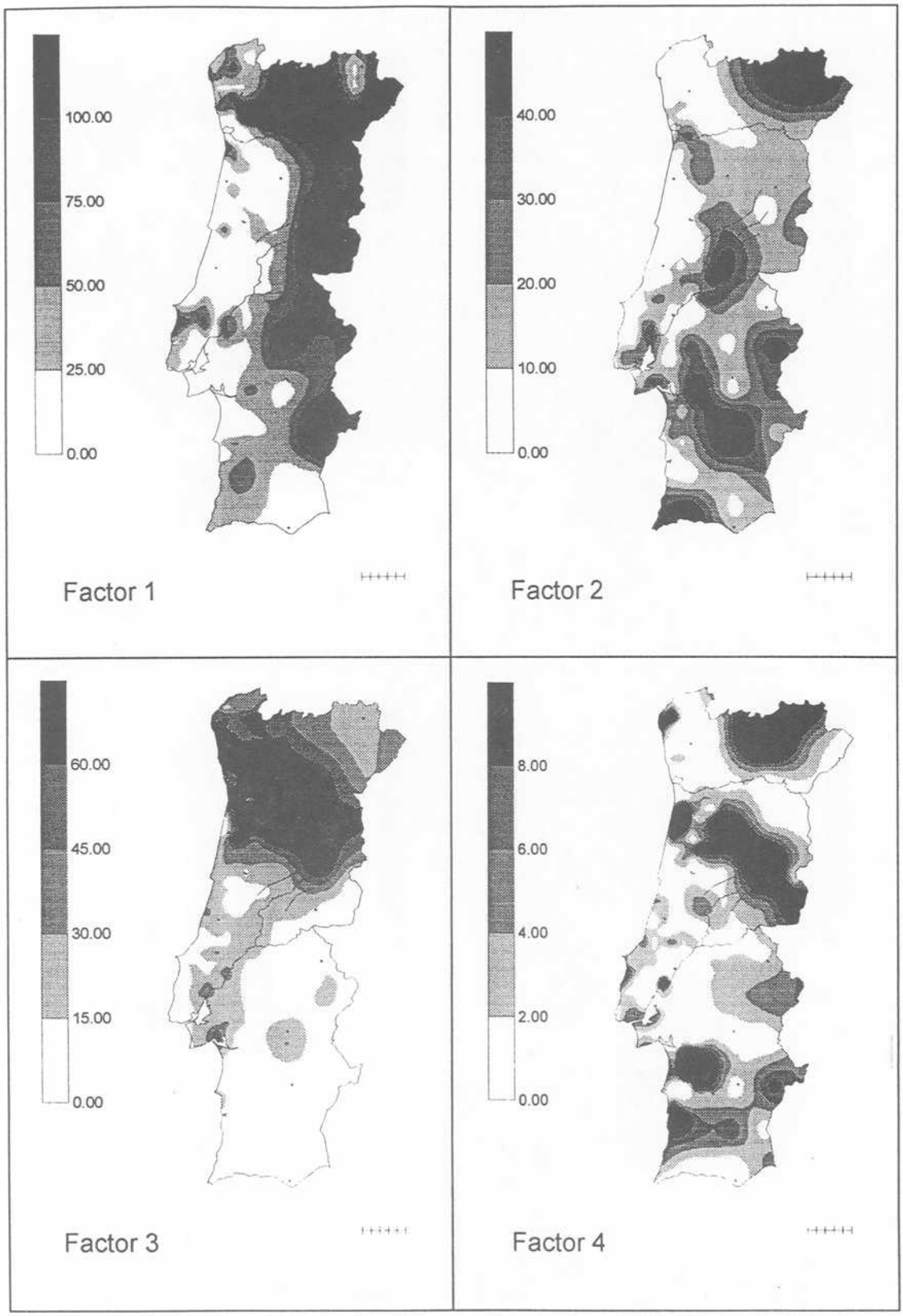

Fig. 2. Factor plots for the factors 1 to 4 obtained from the global data set

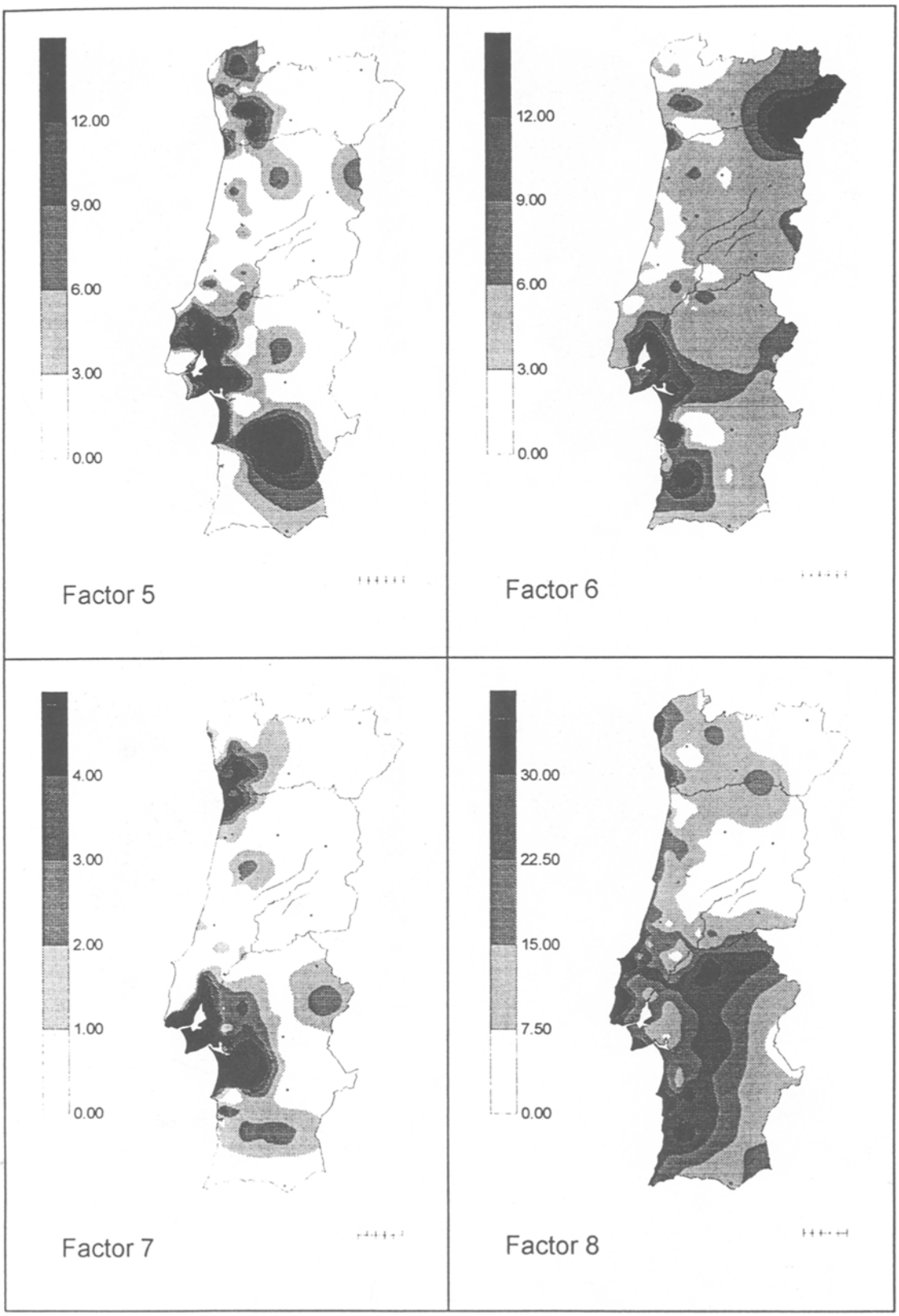

Fig. 3. Factor plots for the factors 5 to 8 obtained from the global data set

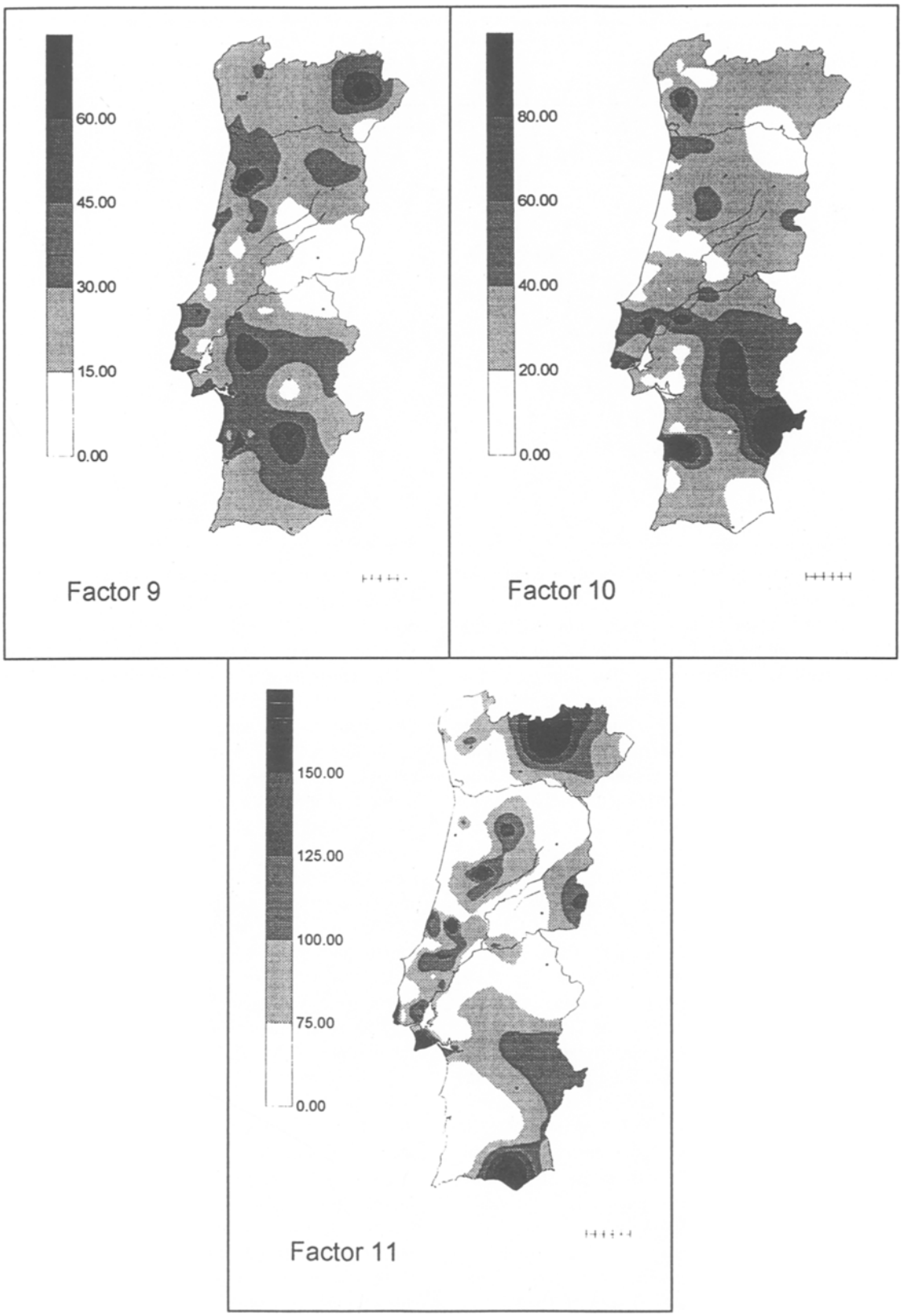

Fig. 4. Factor plots for the factors 9 to 11 obtained from the global data set

Table 4. Cos(N-dimensional vector angles) between Lichens Factors and Nriago 89 mean sources for factors obtained using both INAA and PIXE data. See also Table 2

	Fac 1	Fac 2	Fac 3	Fac 4	Fac 5	Fac 6	Fac 7	Fac 8	Fac 9	Fac 10	Fac 11
WIND	0.96								0.92		
SEAS											
VOLC	0.86								0.87		
FIRE	0.92								0.92		
BIOP											
BIOV											
BIOM											
COAL											
OILE		0.76				0.94					
NFMM				0.77							
PBPR				0.85							
CUNI											
ZNPR			0.91				0.76	0.99		0.99	0.93
SECN	0.98								0.93		
IRON										0.79	0.78
INCE	0.80								0.77		
FOSF			0.94					0.99		0.99	0.88
CEME			0.81				0.95	0.80		0.81	0.99
FUEL			0.88				0.88	0.81		0.81	0.94
VARI				0.82							

represents a contribution 18% to Pb. Factor 4 contributes 40% for W and 14% for As.

Factor 5 (INAA factor 1) does not show any correlation with the mean sources in Table 4. INAA factor 1 is correlated to both Seasalt spray and oil combustion. This strange correlation can be found in the previous work as a factor due to resuspension of material from pyrite manipulation processes. So we interpret this factor 5 (pilot element: Cu) in the same way. It is still important to refer that from the auto-correlation matrix of the global data set factors, a strong correlation (0.97) can be found between factors 4 and 5. Factor 5 contributes 27% for Cu and about 20% for V and Ni.

Factor 6 (INAA factor 5) is correlated to oil combustion, nevertheless it has as pilot element Cl. In fact this factor has 80% chlorine, as shown in Table 3, and is responsible for almost 33% of the Cl variations detected. It is not yet understandable to which kind of source it can be assigned. This factor justifies also 67% of V.

Factor 7 (INAA factor 6) although correlated to cement production mean source, the fact that Ca is not in the composition implies that this is not an acceptable interpretation. Both this factor and INAA factor 6 have Sb as pilot element. INAA factor 6 is correlated to oil combustion sources; KABATA-PENDIAS[9] refers Sb as being originated from industrial environments. The high values of the toxic elements S, V, Ni, Zn, As, and Pb in this factor takes us to believe that this factor is associated to general oil powered industries. This factor has no correspondence in the previous work, it contributes to 34% of Sb and 15% of Pb.

Factor 8 (INAA factor 4) has iodine as pilot element and is highly correlated to phosphate fertilisers and Zn production sources of NRIAGO's (Table 4). KABATA-PENDIAS[9] refers that iodine is used as a fertiliser for soil or foliar application. This factor corresponds to a part of a factor in the previous work which included both phosphate products and traffic activities. This factor gets now better specified as corresponding to agriculture fertilising processes using algae and sewage sludge.[9] Also some contribution from sea can be expected based on the strong I correlation. This can justify some maxima found in the factor values pattern which do not correspond to agriculture activity. Nevertheless most of the factor values maxima are located in known agriculture regions. This factor contributes for 92% of I, 42% of Br, 37% of Na, 20% of Se, 17% of S, Ta and U.

Factor 9 (INAA factors 3 and 9) has Mn as pilot element, indicating a natural source, which is also supported by the correlation with NRIAGO's data. From the Fe/Si ratio it could be attributed to eruptive rocks, but the Mg/Al and the Na/Mg ratios correspond to sandstone rocks. The Al/Si ratio is nevertheless very strange because it is atypical. This factor was also identified in the previous work as a combination of eruptive rocks and a factor of old metamorphic rocks. This factor contributes to 52% for Mn, 24% of Hg and 15–22% for Na, Sc, Cr, Fe, Co, Cu and U.

Factor 10 (INAA factors 6 and 7) has Sr as pilot element. KABATA-PENDIAS[9] refers that high Sr levels may be due to coprecipitation by hidrous Fe oxides. From Table 4 no correlation to natural sources is observed; so a possible interpretation as a soil contribution term can not be established. It is then difficult for us to identify the source which originates this factor. The factor values pattern would lead us to attribute this factor to areas comprising various industry plants behaving as a single point source, as is the case of the complex of Sines, where a strong maximum is found. Nevertheless as can be seen from Table 6 this is a very important pollution source contributing 21% for Hg, 28% for Se, 38% for Br, 15% for As, 22% for Zn, 36% for Fe and Co and 25% for Cr. It is also interesting to note that it does not contribute to Pb nor

Table 5. Average % contribution to total element occurrence for the factors obtained using INAA and PIXE data. Only elements for which there is less than 5% of probability of null concentration in the factor are presented

Element	Fac1	Fac2	Fac3	Fac4	Fac5	Fac6	Fac7	Fac8	Fac9	Fac10	Fac11
Na	12.5	3.82	9.95	0.60		1.77	1.58	36.9	16.9	26.8	
Mg	7.49	5.24	12.9	1.04	1.34				10.7		4.48
Al	19.7	6.50	20.4	1.14	2.22				11.3		
Si	16.8	4.98	5.40	2.19	3.65				9.10	12.2	7.63
P			17.1					10.1			7.93
S			4.96		3.09	0.85	1.77	16.9			6.63
Cl				1.19		32.7 P		8.04			
K	5.26		12.8	0.49		0.52	0.49	5.32	7.31	20.5	
Ca											103.2 P
Sc	13.1	12.5		0.73				4.32	19.8	39.1	5.56
Ti	13.6	8.33		1.96	4.18		1.79		7.71	15.5	13.8
V		13.7			17.2	66.7	6.12				
Cr	4.12	13.2		1.18			1.66		21.6	24.9	
Mn	6.64					3.69			51.5 P		
Fe	12.4	10.8	6.1	0.67	1.80	0.55	2.06	7.32	15.4	35.8	4.24
Co	9.81	13.6		0.42	3.10				16.1	36.7	14.5
Ni		15.2		0.53	20.3	9.63	4.76				
Cu			31.9		26.7 P				35.5		
Zn		2.58	28.7		9.01		3.87	8.32		21.9	14.6
Ga	8.63	24.2 P									14.0
As		5.89	30.2	13.8			9.50			15.4	
Se	6.26	2.24		0.87			1.39	20.6		27.9	
Br								41.7		38.3	
Rb	14.8		31.3 P			0.67					
Sr			11.0			1.25				55.5 P	
Zr	22.1			3.43	9.22						21.5
Sb		6.72					33.7 P				
I		9.08						92.2 P			
Cs	24.6	3.07	30.0	0.59		3.77		12.6		18.1	
Ba	14.7	5.52	14.9			2.37	2.04			40.3	7.51
La	19.6	4.92	17.0	0.97	2.89		1.02	11.8		39.4	
Ce	20.1	4.48	16.0	0.86	2.38		1.12	5.04		34.5	3.28
Nd	38.5 P	4.44				4.18	3.20		10.7	13.6	
Sm	17.8	5.80	14.3	1.13	2.01					22.1	5.57
Eu	15.1	7.62		0.93	2.29		0.96	5.80	10.4	40.7	8.18
Tb	17.3	7.95	7.32	0.77	1.90		0.94	4.60	9.81	37.3	5.13
Lu	18.6	8.17		0.96	3.20				11.9	41.2	5.96
Hf	22.6	4.07	7.58	1.06	4.74			8.33		34.3	5.67
Ta	20.9	4.22	20.7	0.80				16.7	8.34	30.9	
W	14.1			39.7 P		5.56					16.4
Hg					4.48		6.98	10.1	24.3	21.4	
Pb	4.68	5.75	17.8	1.73	6.42		14.6				32.2
Th	28.5		33.6		3.24		1.76	10.9		23.4	
U	26.0		44.3	1.81				17.5	19.0	14.0	

S occurrence. Factor 11 (INAA factor 8) has Ca as pilot element and a 0.99 correlation with cement production NRIAGO's source. This factor is then interpreted as due to cement production industry.

This factor is also well identified in INAA factor 8 and PIXE data in the previous work. It is the main source of Ca justifying its total variation. It also contributes to 32% of Pb and 15–20% of Co, Zn, Ga, Zr and W.

From the above discussion we may refer especially the following conclusions:

(1) factor 2 does not exist as coal combustion in the previous work limited to PIXE data set;
(2) factor 4, correlated to mobile sources, has as pilot element W which is an unexpected result;
(3) factor 6, now identified as a Cl anthropogenic source, was attributed to natural Seasalt spray when only PIXE data was considered;
(4) factor 10, although representing an important pollution source, could not be assigned;

Table 6. Factor assignment

Global data set factor	Assignment	Pilot element	INAA data set corresponding factor	INAA factor pilot element
Factor 1	Shale based soil	Nd	Factor 2	Rb
Factor 2	Coal combustion	Ga	Factor 10	I
Factor 3	Phosphate fertilisers	Rb	Factor 2, 3	Rb, W
Factor 4	Electrical power plant + paper paste industry (?)	W	Factor 3	W
Factor 5	Resuspension of material from pyrite mining	Cu	Factor 1	Sc
Factor 6	Cl source	Cl	Factor 5	Cl
Factor 7	Oil powered industries	Sb	Factor 6	Sb
Factor 8	Agriculture fertilisers	I	Factor 4	Sr
Factor 9	Eruptive rocks and sandstone based soils	Mn	Factor 3, 9	W, Mn
Factor 10	Industry complex (?)	Sr	Factor 6, 7	Sb, Sr
Factor 11	Cement production	Ca	Factor 8	Ca

(5) factor 11, connected to cement production, represents a strong pollution factor in Portugal and was undoubtfully recognised with both data sets.

*

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