Journal of Radioanalytical and Nuclear Chemistry, Vol. 259, No. 1 (2004) 35–40

MCTTFA applied to differential biomonitoring in Sado estuary region

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(Received July 21, 2003)

Transplants of the epiphytic lichen *Parmelia sulcata* were suspended in nylon bags within a rectangle of 15 km wide and 25 km long on a grid 2.5 km×2.5 km in the Sado estuary region. The transplants were oriented towards the wind (F) and opposing the wind (T) and were collected after 3, 6 and 9 months of exposure. Samples were analyzed by INAA and PIXE. Source identification was made by Monte Carlo Target Transformation Factor Analysis (MCTTFA) using three different combinations of data (all data, F data and T data). Five factors were identified for all the combinations performed. For two factors, F and T differentiation was observed.

Introduction

Metal concentrations in lichen thalli and mosses have been shown to correlate with atmospheric levels.[1–7] Different lichen species have already been successfully used for monitoring programmes in several countries on a national and local scale.[8–11] A study using lichen transplants started in 1997 in Sado estuary region (40 km South-East of Lisbon) using differential biomonitoring: transplants facing the wind (F) and opposing the wind (T) in a device built for the purpose for 3, 6 and 9 months exposure. A few publications present the first results obtained.[12–14] In this work, Monte Carlo assisted Target Transformation Factor Analysis[15,16] (MCTTFA) was applied to the data.

Experimental

The trace element monitoring was carried out with epiphytic lichen transplants of *Parmelia sulcata* Taylor. The transplants were suspended in December 1997 according to a grid[17] in the Sado estuary area. They were oriented facing (F) and opposing the wind direction (T). On March 1998, 39 F-transplants and 39 T-transplants (called F3 and T3, respectively) were collected, 34 F-transplants and 34 T-transplants were collected in June 1998 (called F6 and T6), and 25 F-transplants and 31 T-transplants were collected in September 1998 (called F9 and T9). The lichen transplants were analyzed by INAA at the Portuguese Nuclear Research Reactor (RPI, neutron flux $1\cdot10^{13}$ $n\cdot cm^{-2}\cdot s^{-1}$) and PIXE in the Van de Graaff accelerator also at ITN, following the procedure described previously.[12–14,17]

Results and discussion

MCATTFA was applied to the data at IRI (Delft, The Netherlands) using 26 elements: Na, Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sb, Ba, Pb, U. Three data sets combinations were used: all data (F3, F6, F9, T3, T6, T9), facing the wind transplants (F3, F6, F9) and opposing the wind transplants (T3, T6, T9). In order to choose the optimal number of factors in each case, use was made of FIC[15,16] (factor identification conflicts, see Fig. 1). In the case of all data (201 samples used), FIC graph shows some sharp rises at 7, 9 and 10 factors. The total amount of explained variance is 0.74, 0.79 and 0.81, respectively. Also the rejected modified data sets due to assignment conflicts are 0%, 7% and 12%, respectively (all centred in one factor) and so 9 was the optimal number of factors chosen. For the combination of F data (97 samples used), 7 and 10 factors are pointed out and the explained variance is 0.72 and 0.80, respectively. In the case of 10 factors, 12% of the generated modified data sets provided by Monte Carlo were rejected due to factor assignment conflicts (most of them centred in one single factor) and so 7 factors were chosen with only 0.2% of modified data sets rejected. For the T data sets combination (104 samples used), FIC points out to 7, 8 or 10 factors. Total explained variance is 0.82, 0.84 and 0.86 with 2, 4 and 13% of rejected modified data sets respectively. Since in the case of 8 factors, half of this sets were centred in one single factor, 7 was chosen as the optimal number of factors to be used.

Table 1 show the normalized average factor loadings for factor analysis performed with all data. Pilot elements and relative errors are also presented. Three soil factors are identified in factors 2, 4 and 8 with Mn, Sc and Co as pilot elements. Factor 3 was identified as the sea salt spray factor with Cl and Na the elements presenting the highest correlation with the factor.

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0236–5731/2004/USD 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

The Na/Cl ratio obtained of 0.56 equal to the ratio for seawater presented by BOWEN,[18] which was already expected due to the proximity of the sea. The physiological factor is related with the biomonitor itself, in this case the lichen, and can be observed in factor 5 with K and P as the pilot elements and also with Rb associated. According to BOWEN,[18] the P/K ratio for lichen lays between 0.087 and 1.23, which is compatible with the obtained value of 0.28. Factor 1, has Sb, Cu, V, Pb and Ni as the most related elements with very small errors in loadings (4 to 6%). This factor points out to oil combustion (fuel power station present in the region). The Ni/V ratio obtained of 0.54 is close to NRIAGU's value[19] of 0.36 and agrees well with ratios for European aerosol (0.4 to 0.7).[20] Factor 6 has As as the pilot element and Ca, Si, Ba, Al, Rb and Sc as the most correlated elements. This factor was associated with agricultural activities. The northern part of the grid has still intense agriculture mainly wine production with the associated fumigations of pesticides and herbicides in the vineyards. These products are one of the possible sources of arsenic.[1,2,21] Factor 7 has Cr as pilot element and some other correlated elements are Si, Zn, Al, Fe, Sc, S, Ni, Ti and Br. According to NRIAGU[19] and other works,[1,2,22,23] Cr and Zn are the most important elements associated with iron and steel manufacture. The area has several of this type of industries that might be responsible for the emission of these elements. Factor 9 has uranium as pilot element and Ca, As, Se, Sb, Mn, Ba, V, Cu and Na as associated elements. This element association points out to cement production but still the correlation of uranium with this factor is too high. This industry is situated Southwest of the sampling grid but this factor might be a mixture of two different sources.

The use of all data to run MCTTFA was based on the assumption that factor loadings were not depending on time, facing or opposing the wind direction. MCTTFA also run with F3, F6, F9 and T3, T6, T9 separately assuming that the factor loadings were only not depending on time. A comparison between the results provided by the three different combinations was performed by calculating the angles between the factors obtained. The factors can be written as vectors in an n-dimensional space where the co-ordinates are just the elements content. The cosines of the angles marked black correspond to a correlation between the factors higher than 0.75 (Table 2). Comparing the all data factors with the F data factors, 6 to 7 factors are very similar for both combinations since the cosine values range from 0.80 to 0.99. Factor 4 (all data) presents a higher cosine value with factor 7 (F data) than with factor 4 (F data) and so the first correlation was the one considered. Factor 7 (all data) and factor 4 (F data)

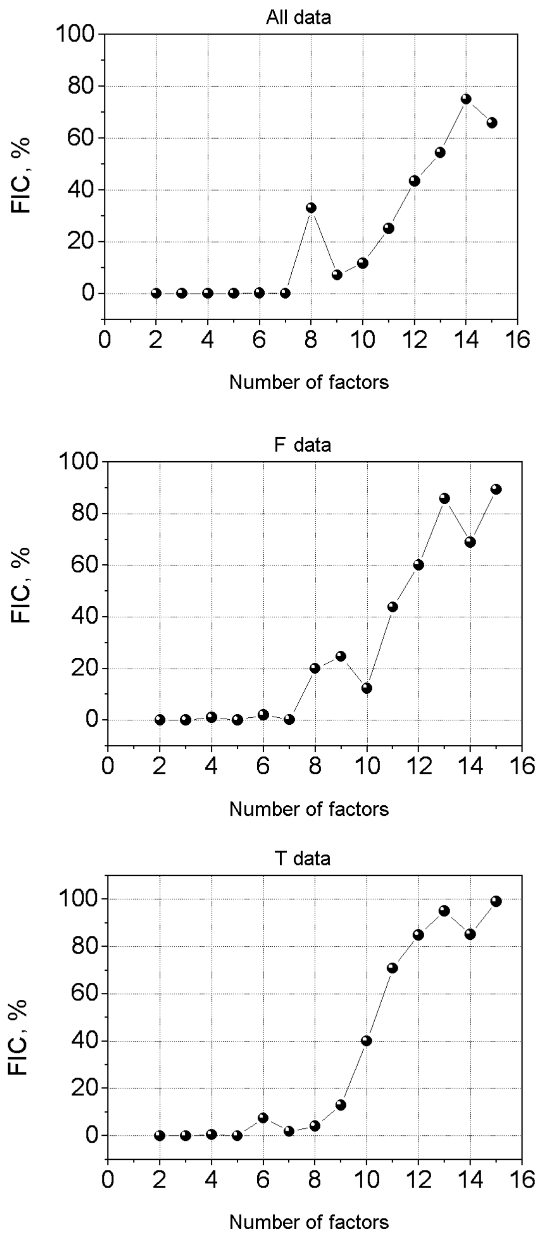

Fig. 1. Percentage of factor identification conflicts (FIC) as a function of the retained number of factors for the three Sado estuary data combinations ran by MCTTFA

Table 1. Normalized averaged factor loadings obtained after 500 Monte-Carlo variations for all Sado data

Element	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7	Factor 8	Factor 9
Na	33361* (27)		56.0* (2)	224857* (24)	9.66* (32)	11811* (33)			36748+ (52)
Al		2949* (7)		103542+ (57)	7.58* (32)	33461* (18)	27352* (10)	57505* (24)	
Si		6312* (8)		311166* (46)		94661* (14)	69614* (9)	140858* (23)	
P		273* (16)			28.0* (2)		2909* (20)		
S	93847* (11)	1387* (8)	22.7* (3)			17572* (19)	10210* (16)	31094* (21)	
Cl		788* (22)	100P (1)		11.1* (45)				
K				80205* (37)	100P (2)	6958+ (44)			
Ca	173412* (28)		61.3* (9)	982766* (19)	24.1+ (42)	148967* (17)			298947+ (41)
Sc	14.4* (13)	0.14* (24)		100P (7)		3.68* (20)	2.98* (15)	10.5* (23)	
Ti		426* (4)		26922* (16)			1245* (13)		
V	1412* (4)		0.05* (7)	455* (39)	0.02* (19)	35.4+ (64)	38.2* (30)		140* (32)
Cr	240* (25)		0.01* (25)	946* (17)			100P (9)		
Mn		100P (3)	0.24* (10)	5021+ (21)	0.32* (24)				954* (37)
Fe	102881* (7)	441* (24)	2.55* (26)	307688* (8)		12742* (15)	14147* (11)	37468* (16)	
Co	93.4+ (31)		0.00+ (33)					100P (6)	
Ni	765* (6)	11.0* (3)	0.05* (5)			36.3* (49)	44.4* (9)	88.8* (47)	
Cu	18776* (7)	101* (7)				1191* (30)		1283+ (94)	1793+ (45)
Zn	25792* (7)		3.31* (4)				4095* (9)		
As	106* (27)	0.84+ (32)	0.00* (31)			100P (5)	5.49+ (58)		89.9+ (41)
Se	16.5* (12)	0.06+ (50)		59.1* (8)					6.07* (39)
Br	1004* (17)		0.37* (5)	3197* (13)			155* (20)		423* (40)
Rb				1238* (8)	0.17* (5)	70.8* (20)		105+ (34)	
Sb	100P (6)	0.22* (13)	0.00* (10)	34.7* (28)			1.33+ (46)	7.43* (77)	12.9* (23)
Ba	1329* (10)	4.62* (30)	0.06* (19)	3019* (8)		267* (10)	67.8* (26)	362* 918)	283* (34)
Pb	3550* (5)	17.9* (7)	0.10* (9)	1040* (34)					
U			0.00+ (51)				2.33+ (42)		100P (12)

Indicated loadings were found to be significantly positive (P>95%), values marked with a * are more than 99% significant and values marked with + are 95–99% significant. Pilot elements are marked with P. Relative errors in percentage are given in parentheses.

present a correlation of 0.80, lower than the others (of 0.90 or higher). In the case of the comparison of all data factors with T data factors, 4 to 6 factors can be considered similar in both combinations (cosines between 0.77 and 0.98). Factor 4 (all data) resembles factor 2 (T data) but the correlation is below 0.90. There is also a similarity between factor 7 in both combinations although correlation is only 0.77. Factors 8 and 9 (all data) do not present any similarity with any of the factors of the two other combinations. This is in agreement with the results obtained for F and T comparison where it was found that 5 factors are similar for both combinations (cosines between 0.87 to 0.96) and 2 factors seem F or T specific with cosine values lower than 0.75. Although factor 4 (F) is similar to factor 2 (T) the correlation with all data is not the same. Factor 4 (all data) resembles more factor 7 in the case of F data and factor 2 in the case of T data. Nevertheless the correlation of factor 4 (all data) with factor 4 (F data) is 0.79, which is a considerable value. Table 3 presents average contributions (%) to total element occurrence for MCTTFA performed with F data and T data, respectively. Observing the fractional variances explained by the factors, for the factors identified as the same in both F and T combinations, it is possible to observe that factors 1, 2 and 5 (F data) have similar strength when compared with the corresponding factors 1, 4 and 5 (T data). Despite the fact that the average contributions of each element might be somewhat different the mean is similar. For instance, for factor 5 the mean of the averaged contributions to total element occurrence is 14% and 12% for F data and T data respectively but K contribution is not the same (77% and 90% for F and T respectively) .On the other hand, factors 2 and 3 (T data) are somewhat stronger than the corresponding factors 4 and 3 (F data) although average contribution values don't differentiate that much.

Table 2. Cos(N-dimensional vector angles) between the MCTTFA factors for the three different combinations performed

A F	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7	Factor 8	Factor 9
Factor 1	0.97	0.36	0.37	0.37	0.03	0.29	0.39	0.51	0.16
Factor 2	0.33	0.99	0.26	0.35	0.14	0.40	0.59	0.40	0.09
Factor 3	0.44	0.25	0.98	0.33	0.05	0.24	0.43	0.18	0.22
Factor 4	0.41	0.37	0.23	0.79	0.15	0.56	0.80	0.74	0.09
Factor 5	0.06	0.17	0.18	0.32	0.97	0.22	0.11	0.19	0.18
Factor 6	0.40	0.41	0.32	0.37	0.17	0.90	0.50	0.39	0.59
Factor 7	0.52	0.38	0.41	0.89	0.19	0.39	0.30	0.31	0.31
A T									
Factor 1	0.93	0.39	0.36	0.43	0.02	0.43	0.38	0.45	0.40
Factor 2	0.39	0.48	0.16	0.84	0.13	0.49	0.70	0.71	0.27
Factor 3	0.40	0.25	0.98	0.26	0.05	0.21	0.30	0.19	0.16
Factor 4	0.38	0.95	0.26	0.32	0.16	0.52	0.61	0.46	0.12
Factor 5	0.04	0.20	0.00	0.35	0.97	0.22	0.20	0.19	0.01
Factor 6	0.42	0.26	0.36	0.51	0.20	0.74	0.17	0.43	0.50
Factor 7	0.63	0.20	0.46	0.43	0.06	0.34	0.77	0.42	0.44
F T									
Factor 1	0.87	0.32	0.36	0.39	0.09	0.50	0.49		
Factor 2	0.38	0.50	0.22	0.88	0.20	0.48	0.63		
Factor 3	0.37	0.25	0.96	0.21	0.17	0.25	0.38		
Factor 4	0.35	0.95	0.24	0.46	0.19	0.53	0.28		
Factor 5	0.05	0.21	0.01	0.27	0.93	0.21	0.26		
Factor 6	0.37	0.23	0.30	0.43	0.36	0.70	0.58		
Factor 7	0.59	0.26	0.54	0.62	0.13	0.49	0.36		

All data (A), facing the wind transplants data (F) and opposing the wind transplants data (T). Only values greater than 0.75 are marked black.

Conclusions

Nine factors were identified using all Sado data sets and seven factors were identified using F and T data separately. The number of samples used (201 against 97 and 104, respectively) might be the reason for this result since the double of samples were available in the first case. Two factors are only identified in all data combination. Five factors were identified for the three combinations performed, oil combustion, 2 soils, marine and physiological factors. The factors identified as agricultural activities and ferrous metal processing and handling, seem to be transplant specific. This means that depending on the positing of the transplant, facing or opposing the wind, they might be more sensitive to certain sources. For these 2 factors, F data presents better correlation with all data than T data. Overall the relative strength of the factors is similar for F and T in common sources.

Table 3. Averaged contributions (%) to total element occurrence obtained after 500 Monte-Carlo variations for facing the wind transplants (F) and opposing the wind transplants (T)

F data Element	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7	Total
Na			28.50*		25.39*	1.44*	37.22*	93
Al		32.86*		36.99*		2.46*		73
Si		29.06*		41.72*		2.69*		74
P		9.23*			43.93*			54
S	1.70*	17.69*	12.44*	16.49*		1.43*		54
Cl		5.49+	34.09P		19.74*			71
K					77.18P	1.09*	7.36+	87
Ca			7.30*	18.98*	15.10*	3.25*	38.61*	85
Sc	1.66*	9.62*	2.69*	44.70P	4.50+	0.92*	23.60*	88
Ti		60.35P		13.04*			29.35*	103
V	9.98*		13.35*	27.56*	5.39*	1.29*	34.34*	93
Cr			5.06*	76.61*				92
Mn		49.23*	4.13*		24.74*		31.31*	110
Fe	2.88*	9.60*	3.18*	45.41*		1.09*	22.17*	86
Co	7.08*			71.67*	22.70*			103
Ni	5.53*	50.74*	10.46*			1.60*		81
Cu	21.66P	50.85*				6.53*		110
Zn	8.50*	18.84*	32.67*	50.60*		2.79*		124
As		16.68*				15.96P		77
Se	0.44+			10.29+			42.47P	56
Br	0.84*		15.23*	7.63+			30.09*	54
Rb	0.31+			29.90*	34.10*	0.84+	17.20*	84
Sb	12.23*	12.08+	4.65*				47.85*	83
Ba	3.31*	4.10+	4.13*	43.38*	8.30*	1.99*	33.53*	99
Pb	8.88*	16.30*	4.51*			1.46*	25.53*	62
U			11.48*	0	63.12+	13.32*		115
Mean:	5	15	8	22	14	2	21	85

F data Element	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7	Total
Na	1.16*	15.08+	69.41*			17.70*		108
Al		49.51*		31.52P	13.31*		0.68+	96
Si		48.32*	0.03	29.67*	7.30*		0.95*	89
P				13.02*	73.82*		0.42+	91
S	1.96*		17.67*	18.02*		2.57+	0.77*	43
Cl			65.31P	4.99*				78
K	0.23+				90.05P	2.64+		93
Ca	1.28+		11.64*			37.61P	1.91*	60
Sc	1.39*	85.09P			15.34*	6.52*	1.17*	113
Ti		48.51*		28.60*	14.89*			95
V	12.18*		10.77*		4.40+	22.68*	9.70*	60
Cr	4.71*	71.40*	5.09*	12.46*			6.59*	102
Mn			4.79*	30.26*		14.65*		60
Fe	2.66*	79.50*	1.97+	5.98*	4.03+	5.62*	3.20*	103
Co	4.22*	53.15*	6.40*	7.73*		16.85*	2.73*	91
Ni	5.47*	26.93*	18.90*	38.90*			1.12*	92
Cu	19.46P			67.28*		26.44*		123
Zn			60.42*	10.29			29.51P	116
As	7.57*	24.88*		29.74*		47.02*	2.37+	112
Se	3.42*	49.42*			9.80*			68
Br	1.69*	32.72*	26.85*				3.45*	69
Rb		43.26*			55.67*	13.41*		113
Sb	14.33*	20.51*	13.01*	6.52+		10.21*	6.77*	72
Ba	3.69*	49.17*	4.11+	9.57*		23.52*	1.93*	93
Pb	6.60*	7.98+	16.99*	23.66*		4.51+		61
U	2.79*	47.28*				13.09*	5.27*	75
Mean:	4	30	13	15	12	11	3	88

Indicated loadings were found to be significantly positive (*P*>95%), values marked with a * are more than 99% significant and values marked with + are 95–99% significant. Pilot elements are marked with P. Total fraction is given in percents.

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