

A GRAPHICAL TECHNIQUE FOR DISTINGUISHING PLANT MATERIAL AND SOIL FROM ATMOSPHERIC DEPOSITION IN BIOMONITORS

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Abstract

The paper explores the limits to which a new graphical technique can distinguish the various hierarchical levels of sources of trace elements within biomonitors. When applied to data from Portuguese lichens, it appears to resolve four levels of sources, from plant material down to individual types of pollution. Careful factor analysis appears to offer very similar results, being weaker than the graphical method in some aspects and stronger in others. As a result, it now seems possible to determine sources for elements in lichens with better precision and confidence than was available previously.

1. BACKGROUND

1.1. Genesis of this study

This study is an attempt to apply to biomonitors a graphical technique for distinguishing components of elements in environmental media that I have been exploring for the past few years [1]. After developing the technique as a way to deduce the composition of the crustal component of the aerosol from the aerosol itself, I found that it also worked for precipitation, streamwater, soils, stream sediments, marine sediments, and even coal. Having in the meantime become familiar with elemental data for Russian mosses,¹ I wondered whether the technique could be used there, too, perhaps to help address the longstanding problem of distinguishing plant material from deposition. Although the first results were encouraging, they were limited by the small numbers of samples available.

After I had been invited to describe the technique further at this workshop, correspondence with Dr. M.C. Freitas revealed that she had a large, high-quality elemental data set for Portuguese lichens, supplemented by data on deposition and soils throughout Portugal, that she would be willing to share with me. These data have proven so satisfactory that I will focus my entire talk on them.

1.2. The graphical technique

The graphical technique is binary, that is, it separates two components of a mixture at a time. A log-log scatter diagram of a large data set is constructed, with the vertical axis being the crustal ratio of some element X (i.e., X/Al , where Al is the crustal reference element) and the horizontal axis being the ratio to Al of the reference element in the other source (say, Na for the sea or Se for pollution). This form of the horizontal axis creates a crustal left end and, depending on the other element being used, a marine or pollution right end. Thus the more crustal a sample is, the farther to the left of center it will be located, and the more marine or pollution the sample is, the farther to the right it will be located. Given enough samples and a great enough range of compositions, clear crustal and marine or pollution ends can be created. At the crustal end, a horizontal crustal "tail" appears and frequently points asymptotically to the X/Al ratio of the pure crustal component of the samples. At the marine or pollution end, a second asymptotic tail appears, having unit slope. It represents the pure marine or pollution component of the samples, i.e., the other component represented on the horizontal axis. Thus a single plot extracts the compositions of two pure components in mixed samples.

¹ Data generated by Dr. M.V. Frontasyeva of the Joint Institute for Nuclear Research, Dubna.

1.3. Applying the graphical technique to biomonitors

The simplest way to apply the graphical technique to biomonitors is to distinguish the plant component from atmospheric deposition. Plant material can be represented by K or some other element enriched in plants relative to aerosol (Rb, Cs, Sr, and Ca are obvious possibilities), deposition by Al (which has crustal and pollution components in deposition). Using Al allows us to keep X/Al on the vertical axis and use K/Al for the horizontal axis. The resulting plot would have an atmospheric left end and a plant right end.

2. BASIC GEOCHEMISTRY OF THE PORTUGUESE LICHENS

2.1. The data sets

The basic data set consisted of 235 lichen samples taken over all Portugal during July and August 1993. Sampling grids of 10 km x 10 km were used near the coast and 50 km x 50 km in the interior. Samples were analyzed by INAA and TTPIXE; 44 elements were reported. Details are given in Freitas, Reis, Alves, et al. [2]. The data set for soils was generated from 89 samples taken throughout Portugal along with the lichens and analyzed by INAA at ITN (Dr. Isabel Prudencio; see paper by Prudencio et al. in these proceedings). Data for total deposition consisted of annual-average concentrations taken in duplicate at six sites in Portugal. Samples were taken monthly with funnels and plastic bottles and analyzed by ICP-MS at the Geological Survey of the Netherlands (Dr. Bertil van Os).

2.2. Choosing the reference element for plant material in the lichens

The easiest way to choose the best elemental indicator for plant material in the Portuguese lichens is to compare their average composition with that of atmospheric aerosol or deposition. Figure 1 does this by showing elemental enrichment factors of the average lichens relative to average urban aerosol [3], where the enrichment factor of element X is defined as $[X/Al]_{\text{lichens}}/[X/Al]_{\text{urban aerosol}}$. Phosphorous is most strongly enriched in lichens relative to aerosol, and has enrichment factors of 6–7. Below P comes a series of elements with enrichments near unity (K, Ca, Rb, Sr, Cd (artifact of data), REE, Hf, Th, U) and a series of elements depleted by factors of up to 10–100 (the “transition elements” V–Br plus the pollution elements Sb, Hg, and Pb). These results imply that relative to aerosol or deposition, P will be the clearest indicator of plant material, and perhaps the only clear indicator, that a small number of additional elements may be mixtures of plant and aerosol, and that most other elements will come mostly from the aerosol (or deposition). Note that the conventional indicator for plants, K, is predicted to be a distinctly poorer reference element for plant material in these lichens than is P. Therefore, we tried P rather than K as our reference element for plants. The best indicators for deposition are predicted to be Pb and Sb, with Cu, Zn, Se, Br not as good. Overall, the plant contributions to elements in the lichens are predicted to be small.

2.3. Finer levels of discrimination

Distinguishing plant material from atmospheric material within lichens is not the only possible application for the graphical technique. The atmospheric material is itself composed of two components: windblown local soil and true atmospheric deposition, both wet and dry. Atmospheric deposition typically contains three major components: crustal, marine, and pollution. The pollution component itself typically contains contributions from coal combustion, oil combustion, traffic, incineration, industry, etc. Each component of this entire hierarchy, comprising at least three levels below the basic plant-atmosphere pair, is potentially separable graphically.

Portuguese lichens vs urban aerosol

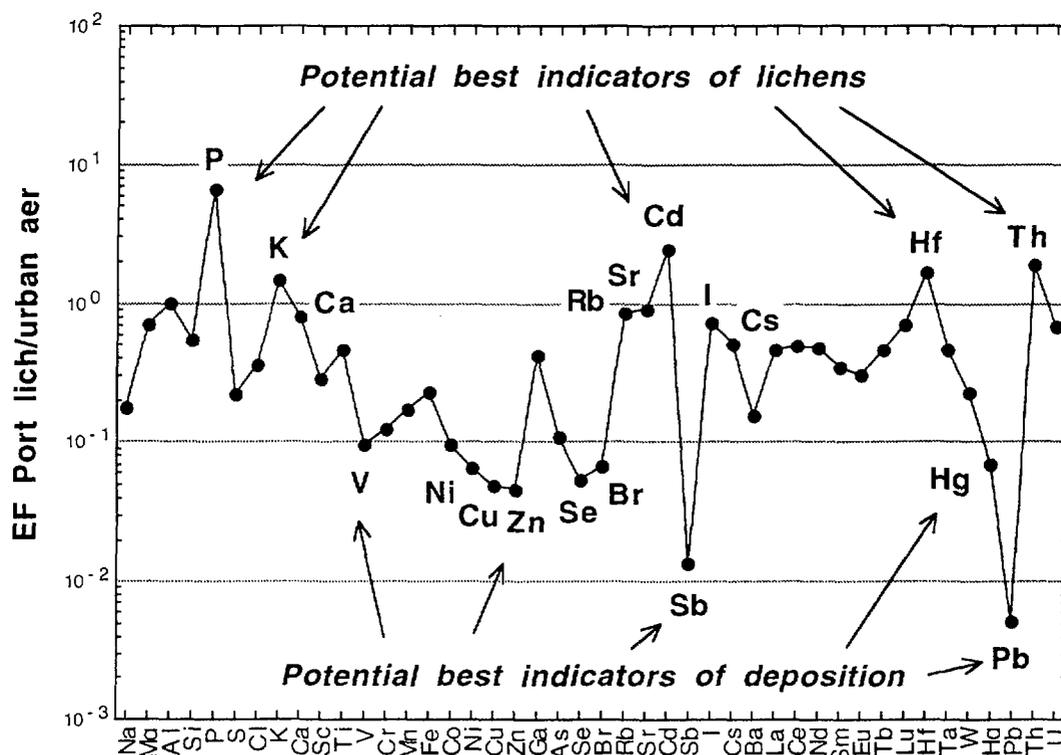


FIG. 1. Enrichment factors of elements in Portuguese lichens with respect to urban aerosol.

2.4. Goals and assumptions of this work

There were three main goals for this exploratory work. The main goal was to see whether the plant and atmospheric components of Portuguese lichens could be distinguished graphically, qualitatively and perhaps even semiquantitatively. (True quantitative resolution will be the next step.) The second goal was to see whether we could distinguish the finer levels of components: the soil and depositional components of the atmospheric component; the crustal, marine, and pollution components of the depositional component, and the coal, oil, and other components within the pollution component. The third goal was to see how the graphical results compared to results from factor analysis.

The major assumption of this exploratory work is that elemental ratios of the atmospheric components of lichens are the same as in the soil and the deposition, i.e., that the elements are deposited to the lichens with the same efficiency and are retained by the lichens to the same degree. Although this assumption is almost certainly violated at times, the extent of the violations and their practical effects on the discriminations will have to wait for later, more quantitative treatment of the data.

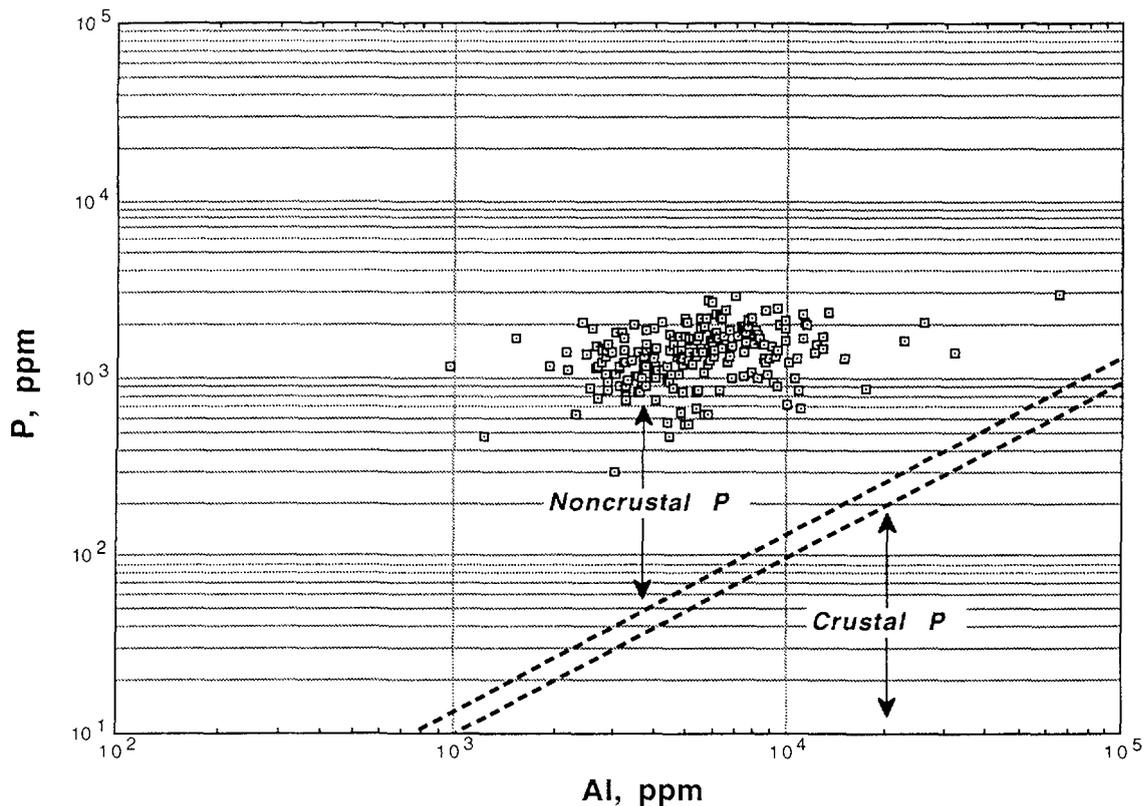
3. CAN WE GRAPHICALLY DISTINGUISH PLANT AND ATMOSPHERIC COMPONENTS?

To distinguish the plant and atmospheric components of the lichens requires two steps. First we use scatter diagrams of one element versus another to confirm that the suspected plant elements do indeed come from plants. Then we use scatter diagrams of elemental ratios to search for plant and atmospheric tails, from which we can estimate the compositions of those components.

If the predicted plant elements truly represent plant material, they must meet three criteria: They must have narrow ranges of concentrations relative to atmospheric elements, they must be enriched relative to atmospheric elements, and they must be in plant proportions with each other.

Text cont. on page 57.

P and Al in Portuguese lichens



K and Al in Portuguese lichens

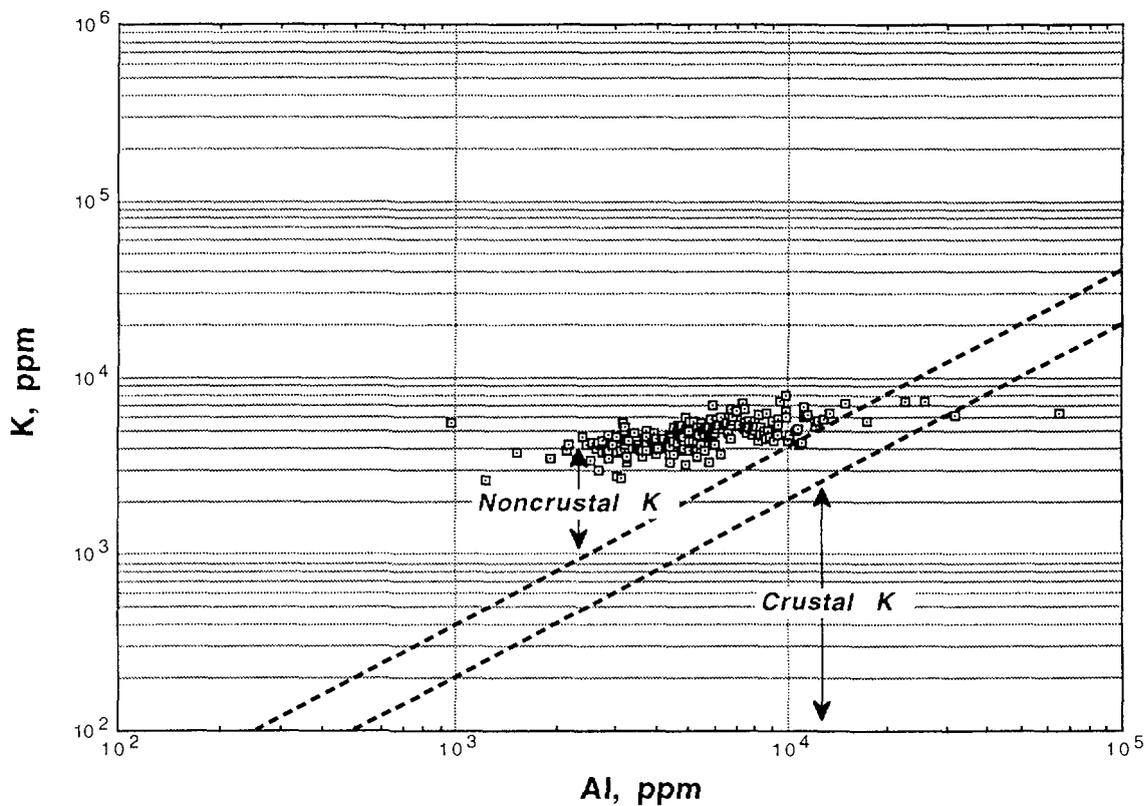
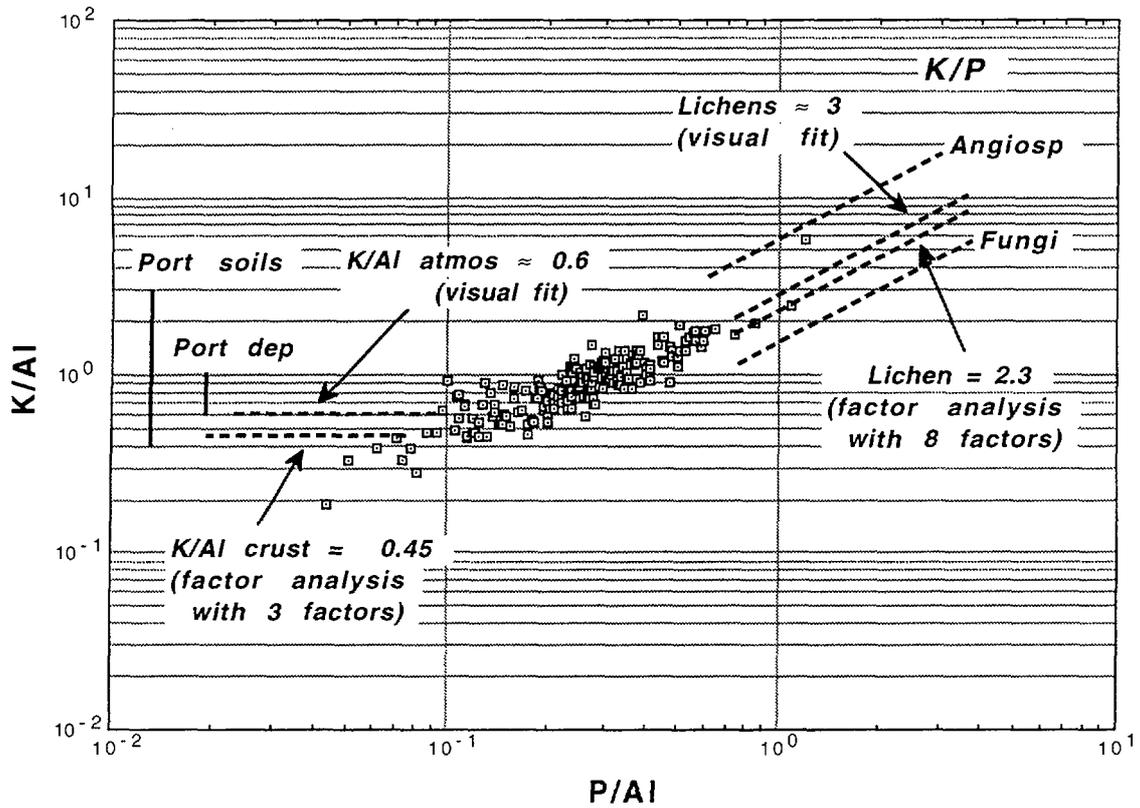


FIG. 2. Scatter diagrams of P vs. Al and K vs. Al in Portuguese lichens.

Portuguese lichens



Portuguese lichens

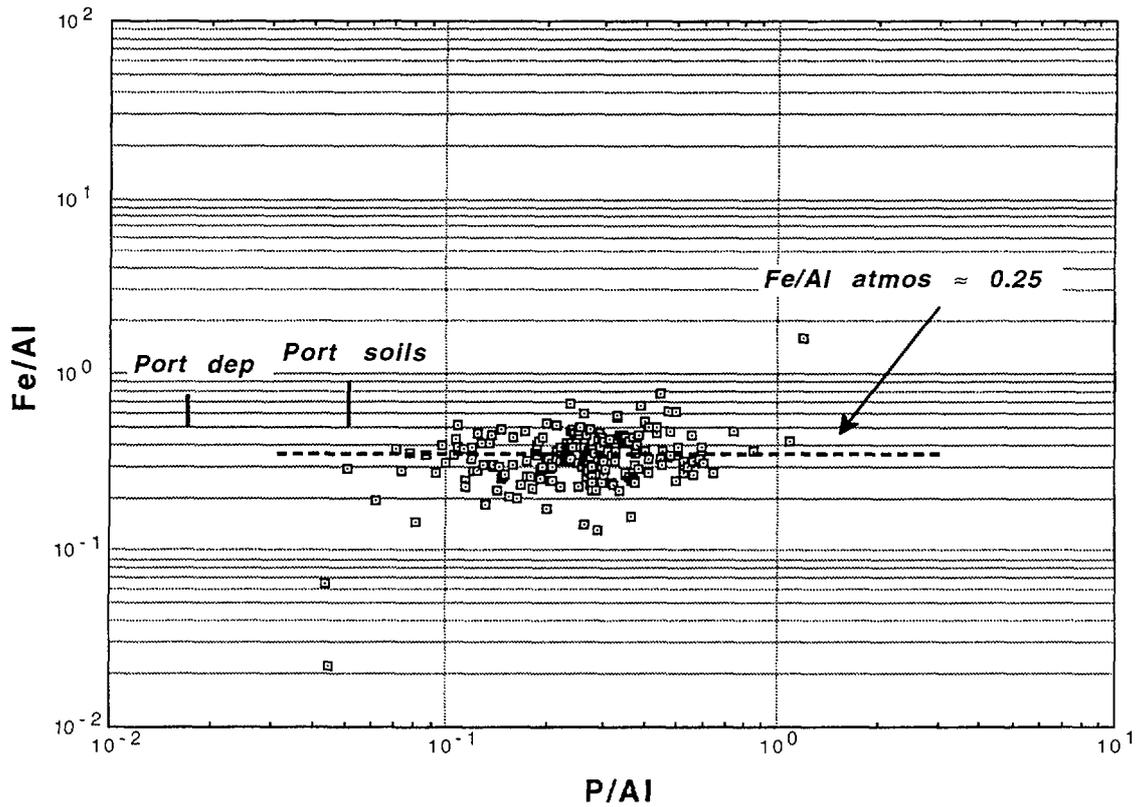
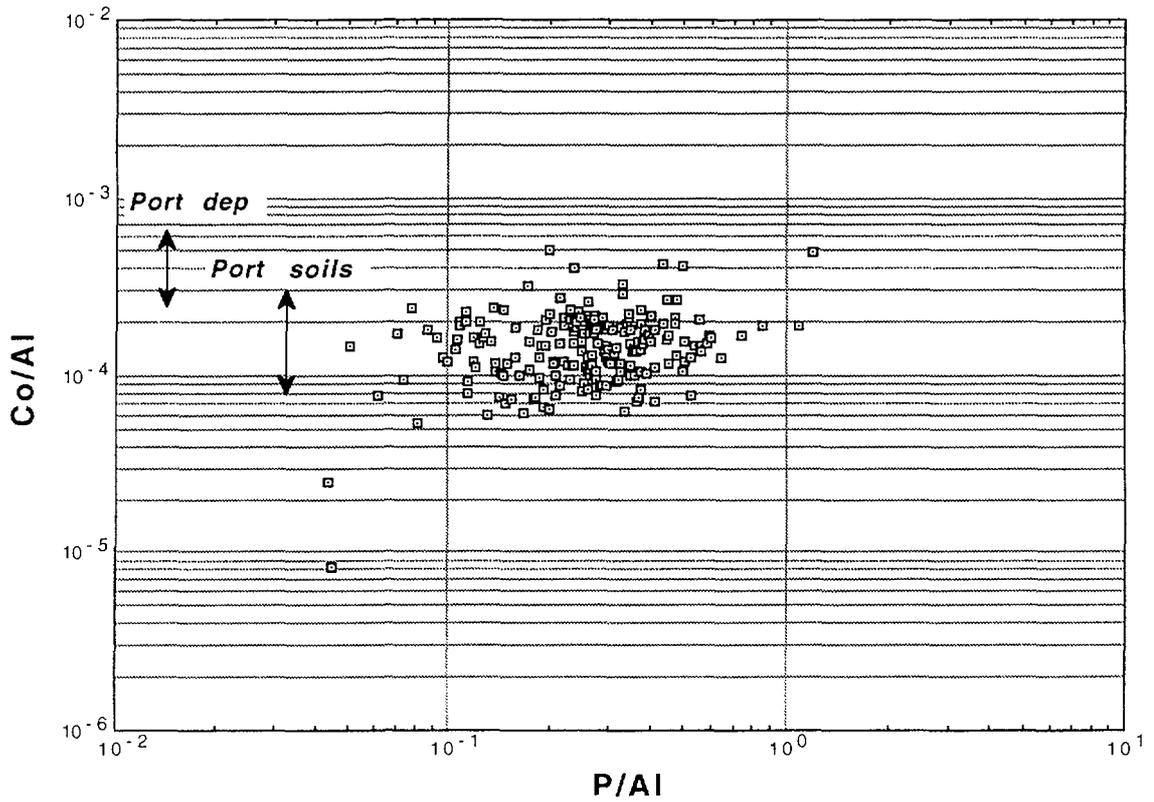


FIG. 3. Scatter diagrams of K/Al vs. P/Al and Fe/Al vs. P/Al in Portuguese lichens.

Portuguese lichens



Portuguese lichens

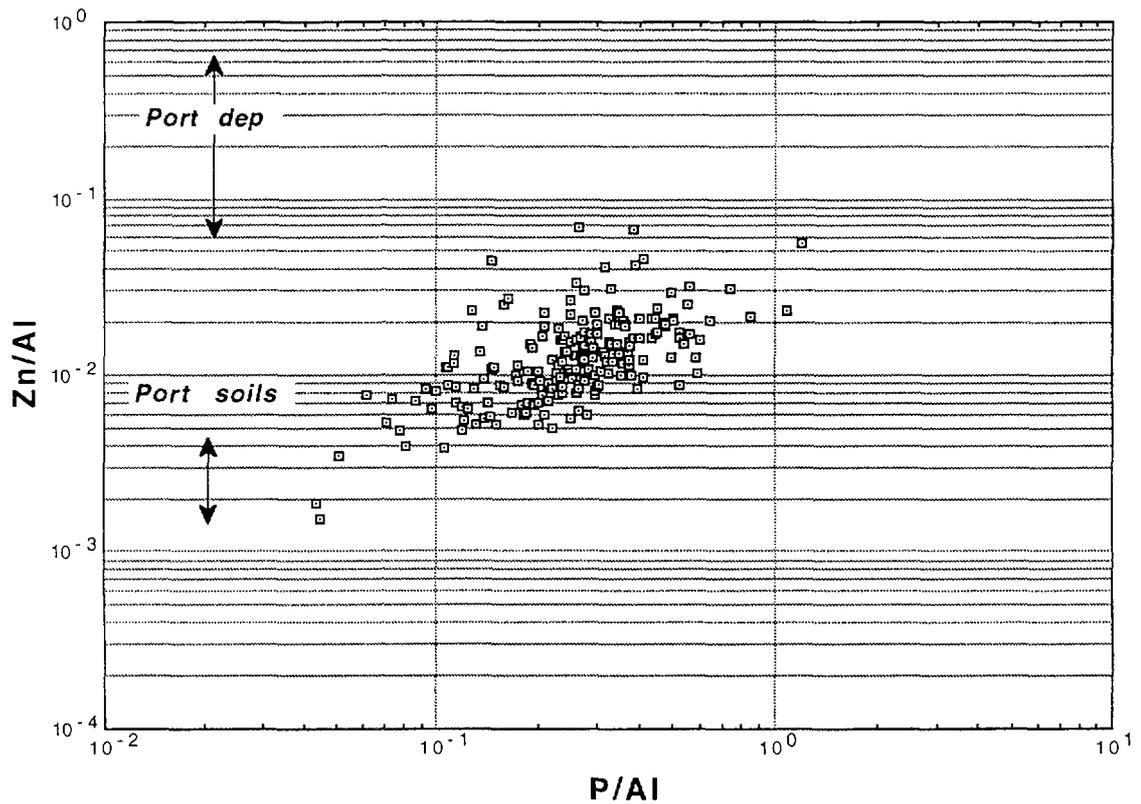
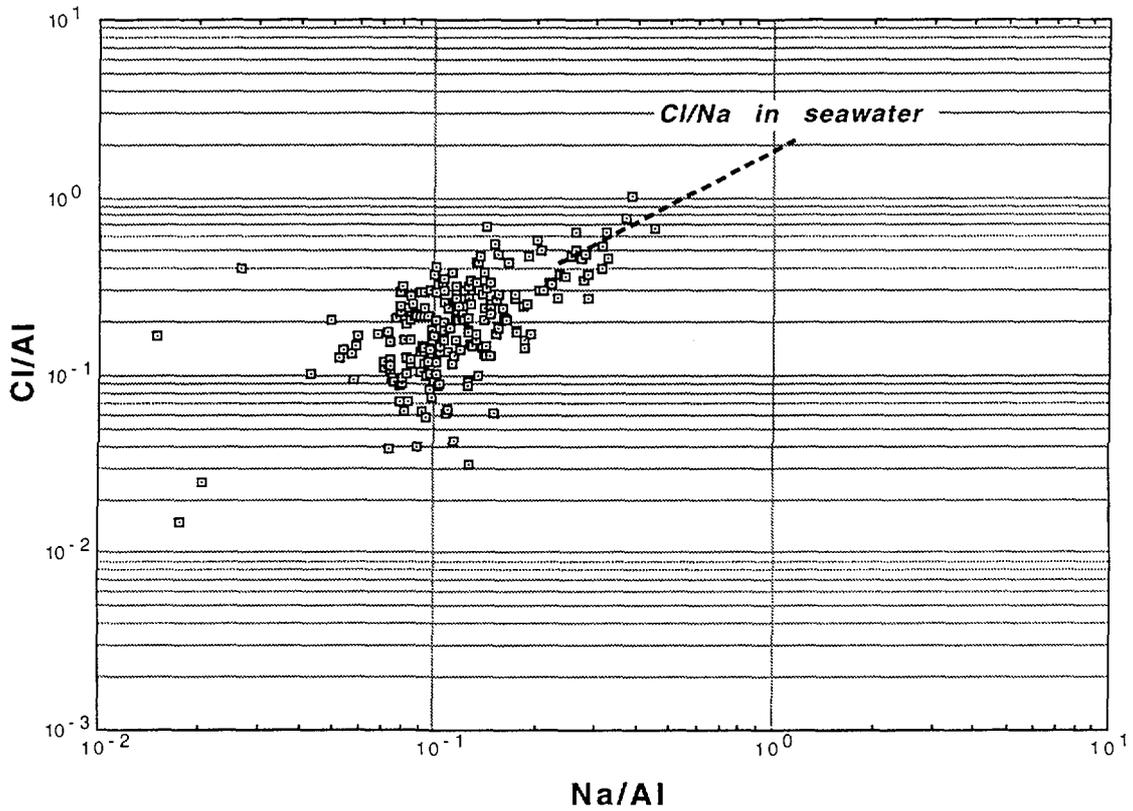


FIG. 4. Scatter diagrams of Co/Al vs. P/Al and Zn/Al vs. P/Al in Portuguese lichens.

Marine component of Portuguese lichens



Marine component of Portuguese lichens

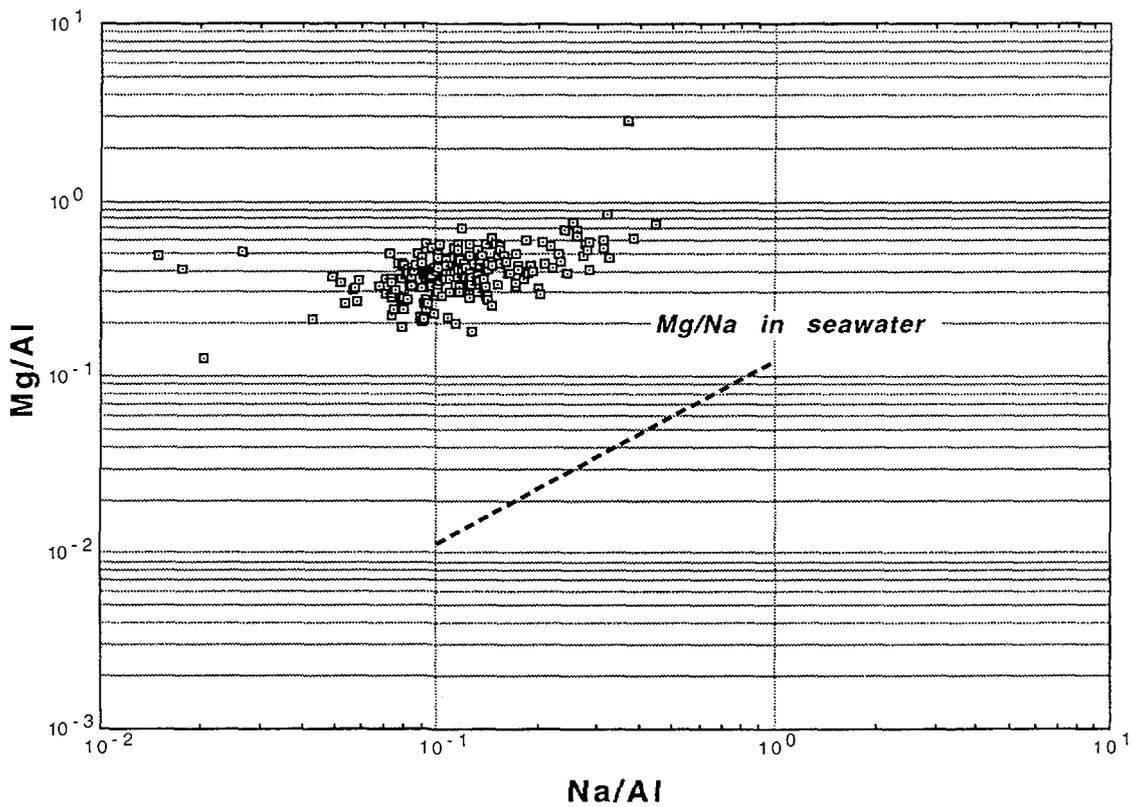
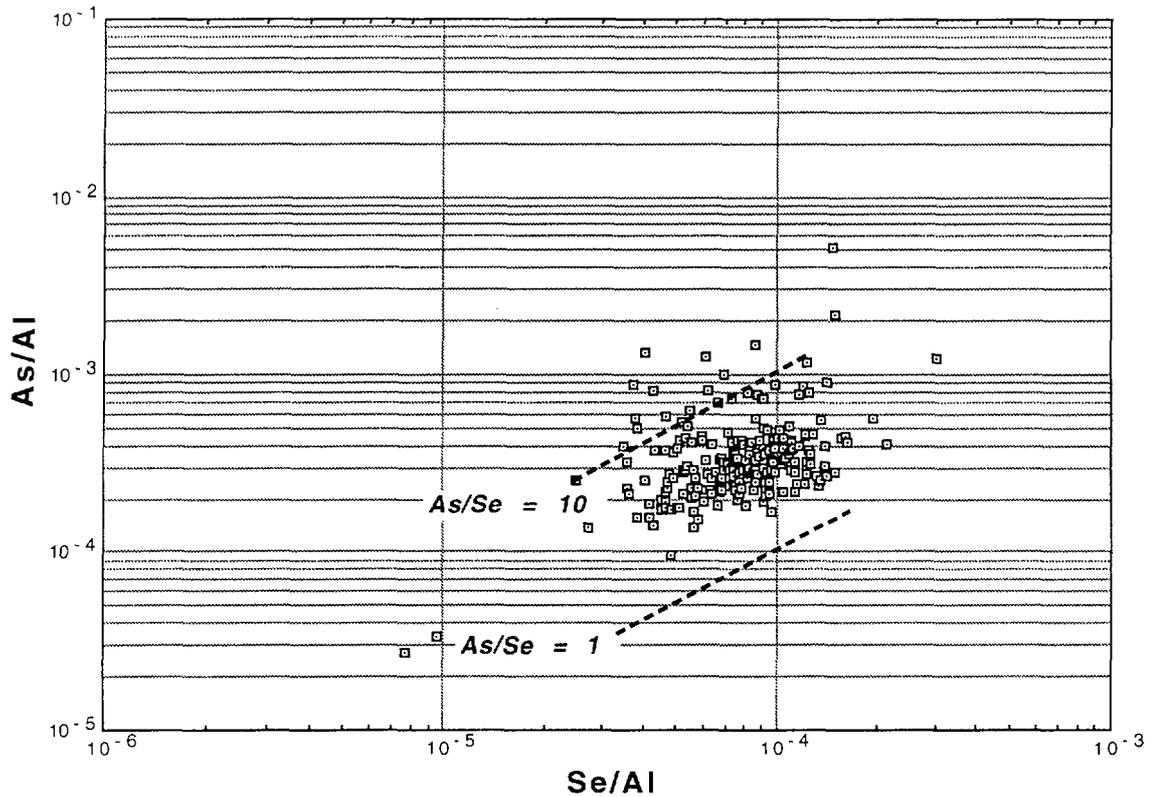


FIG. 5. Scatter diagrams of Cl/Al vs. Na/Al and Mg/Al vs. Na/Al in Portuguese lichens.

General pollution of Portuguese lichens



Oil component of Portuguese lichens

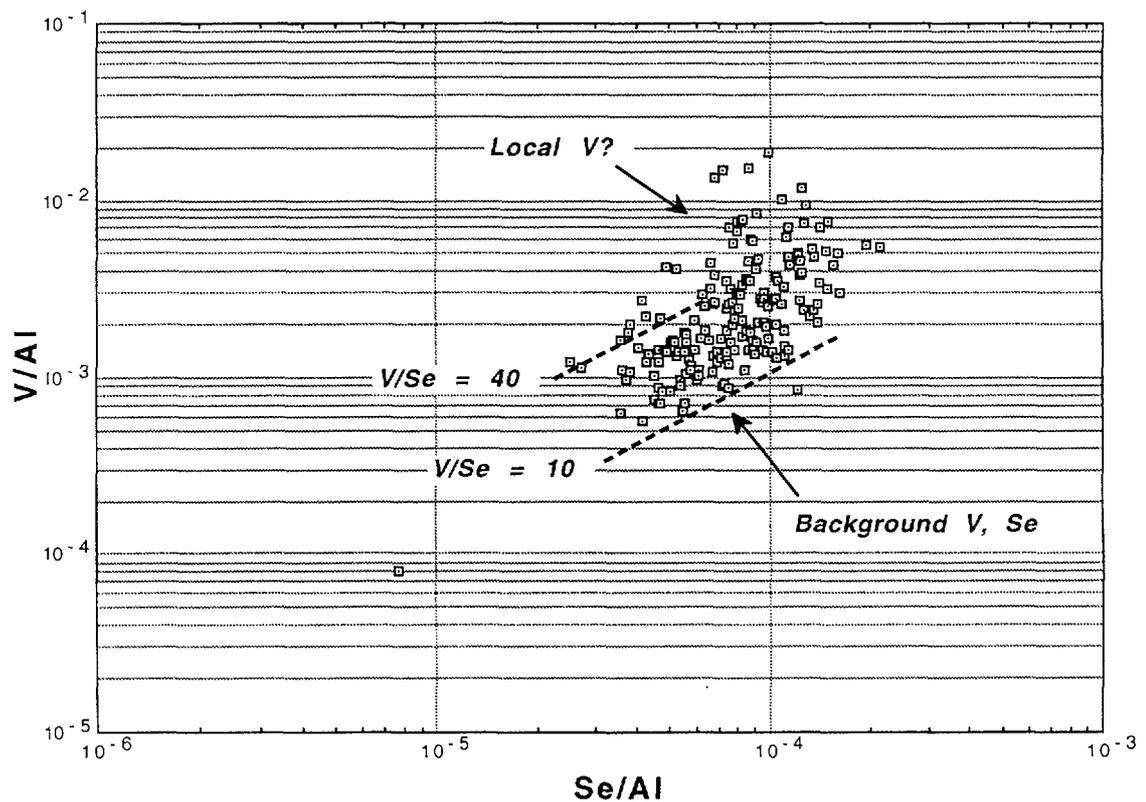
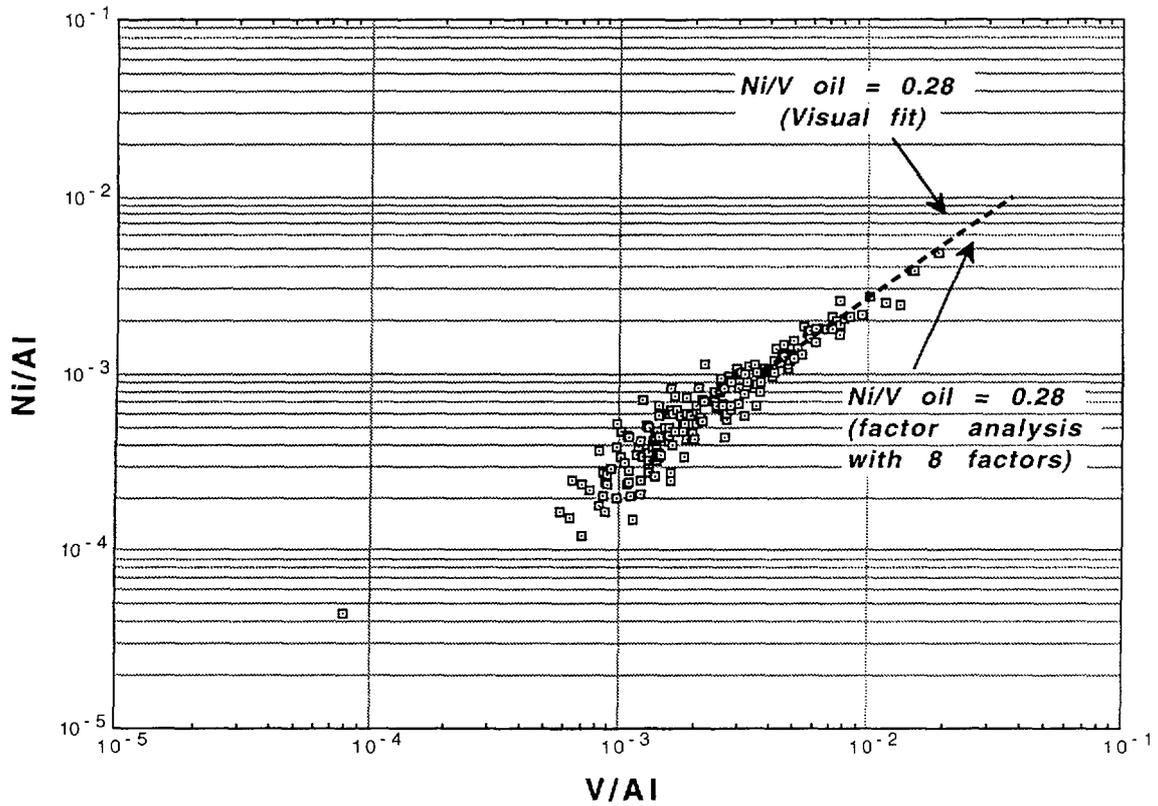


FIG. 6. Scatter diagrams of As/Al vs. Se/Al and V/Al vs. Se/Al in Portuguese lichens.

Oil component of Portuguese lichens



Oil component of Portuguese lichens

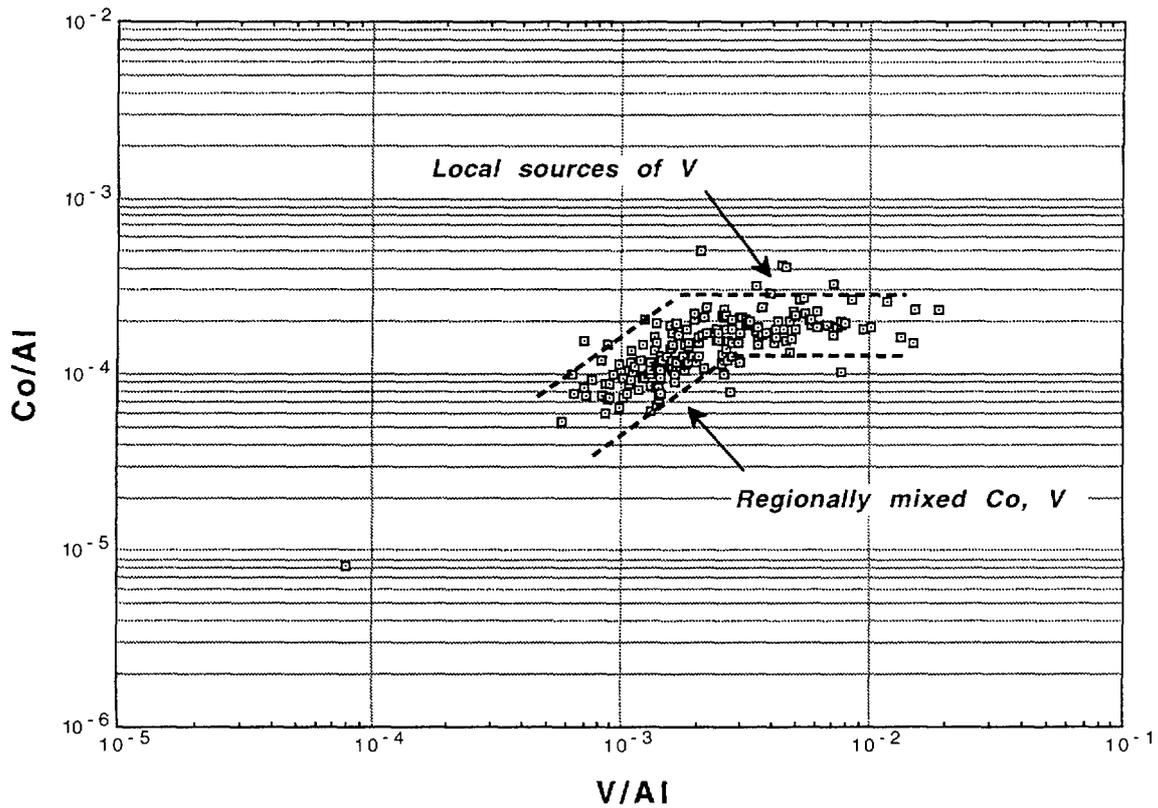
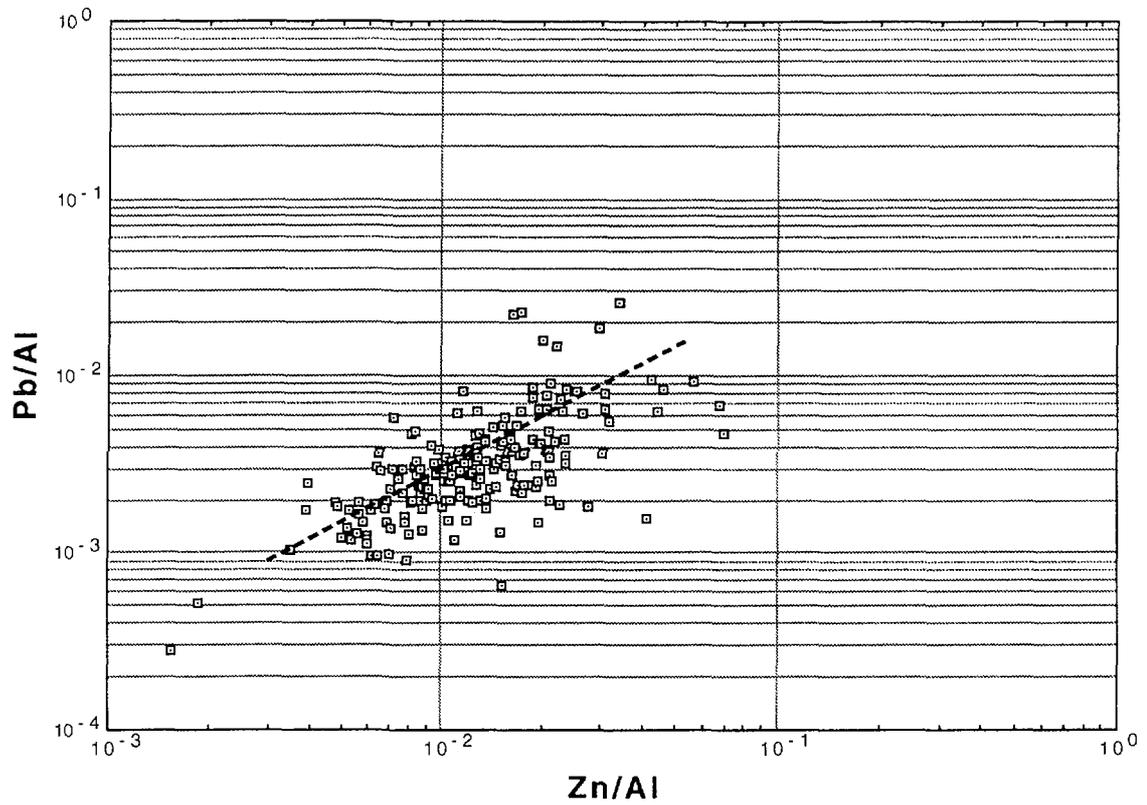


FIG. 7. Scatter diagrams of Ni/Al vs. V/Al and Co/Al vs. V/Al in Portuguese lichens.

Pb and Zn in Portuguese lichens



Cl and Zn in Portuguese lichens

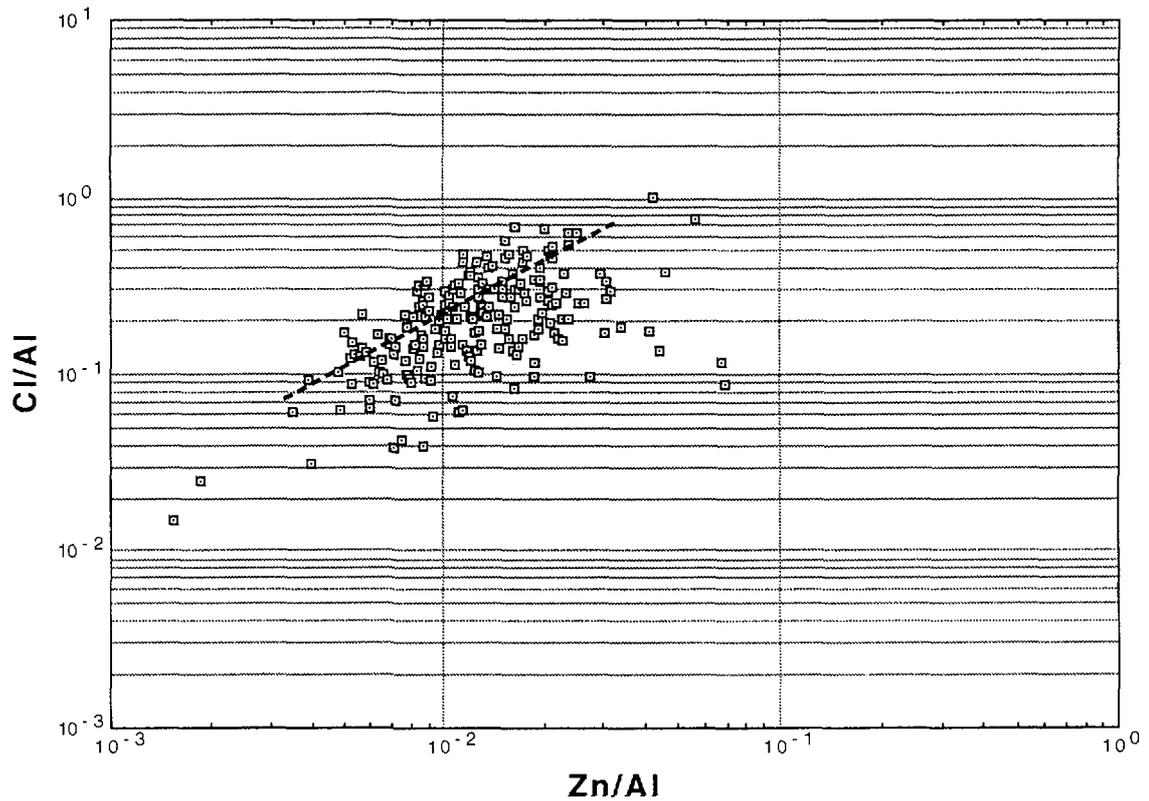


FIG. 8. Scatter diagrams of Pb/AI vs. Zn/AI and Cl/AI vs. Zn/AI in Portuguese lichens.

The first two of these conditions can be checked from plots of the elements versus Al, the third from plots of plant elements versus one another. Figure 2 shows plots for P and K, which from Figure 1 appeared to be the best indicators of plant material, versus Al. Dashed lines indicate the zones of crustal ratios for each pair, as derived from bulk crustal rocks and soils compiled in [3]. Each element has a much smaller range of concentrations than does Al—factors of 2–3 for the elements vs 5 for Al. Each is clearly enriched relative to the crust—typically by a decade for P and by factors of two or so for K. As a bonus, each element shows a clear horizontal tail at low Al, which indicates a substantial nonatmospheric component for each. Thus P and K meet their first two criteria for being plant elements. Although P's graph is noisier than K's, P's greater enrichments relative to the crust would make it a superior indicator of lichens. The third criterion can be addressed by a scatter diagram of K vs P that also shows their concentrations in bryophytes and angiosperms (not shown here). The elements are tightly associated, with nearly all points for each element falling within the range of the two types of plants. While this test is imperfect, it does reassure us that P and K are likely lichen elements.

Plots for two other potential plant elements, Ca and Rb, were less persuasive. Ca, while essentially horizontal, was very noisy and closer to crustal proportions than even K was. Rb's pattern was parallel to the crustal zone and extending into it, which presumably meant that it was strongly crustal and without a detectable plant component. S was a puzzle, being horizontal but well below the zone shown by precipitation in Narragansett, RI. The plot for Sb fell in the zones for Portuguese deposition and Portuguese soils and was parallel to them. After considering these elements and others, I concluded that P and K were the best indicators for plant material in Portuguese lichens, with Ca and possibly S running a distant second.

The second step in distinguishing plant and atmospheric components uses scatter diagrams of X/Al versus P/Al. Plant components of X will appear as tails of unit slope on the right, atmospheric components as horizontal tails on the left. For the Portuguese lichens, K shows the best plant tail, followed by less-distinct tails for S and possibly Ca. Of these elements, only K shows a clear atmospheric tail. Rb, Sr, and Cs show no clear tails, and so appear to be of mixed origins. Pure atmospheric patterns (single long, narrow horizontal tails) are shown by the classical crustal elements (in aerosol) Sc, Fe, Co, the rare earths, etc. Patterns for pollution elements (in aerosol) such as Mn, Zn, As, and Se were generally nearly horizontal, with greater vertical scatter for those elements most pollution-derived in aerosol. Figure 3 shows the plots for K and Fe. The plot for K also depicts rough values for the atmospheric tail ($K/Al = 0.6$) and the plant tail ($K/P = 3$). Note how the atmospheric tail falls within the ranges of the Portuguese soils and deposition and how the lichen tail falls between the values for angiosperms and fungi [4]. For Fe, I have estimated the atmospheric Fe/Al ratio to be about 0.35. The upper end of the zone of points overlaps the ranges of Fe/Al in Portuguese soils and deposition. The Fe plot shows no indication of a plant tail.

4. CAN WE DISTINGUISH SOIL FROM DEPOSITION WITHIN THE ATMOSPHERIC COMPONENT?

Within the atmospheric component of lichens, deposition can potentially be distinguished from soil by the large suite of pollution elements enriched in deposition relative to soil by factors of 10–1000 or more. One need only examine the atmospheric ends of plots of X/Al versus P/Al (or the entire plot if there is no plant component) to see whether the X/Al ratios correspond to the lower values in soil, to the higher values in deposition, or to some combination of the two. A practical limitation to this step was that only eight good pollution elements were available for Portuguese deposition (Mn, As, Sb, Zn, Cu, Ni, Cr, Co), three of which were not available in Portuguese soils (Mn, Cu, Ni). Thus, conclusions distinguishing soil from deposition had to be drawn largely from the five pollution elements As, Sb, Zn, Cr, and Co. (Because Al was not available for the soils, it was estimated as $5000 \times Sc$.)

Plots for these elements indicated that their sources were mostly soil plus some deposition (Cr and Co), similar parts soil and deposition (Zn, Sb), and soil or deposition (As). Thus it appears that both sources can be detected in lichens, with the relative contributions of deposition depending on the degree of enrichment over soil in the deposition. For example, Zn and Sb would have greater contributions from deposition than Cr and Co would have because the former are much more enriched

butions from deposition than Cr and Co would have because the former are much more enriched in aerosol and deposition. The plots for Co and Zn are given in Figure 4. The points for Co extend throughout the range of Portuguese soils and into the lower end of the range for Portuguese deposition. By contrast, nearly all the points for Zn fall above the range for soil but below the range for deposition.

To quantify the relative contributions of soil and deposition to the various elements, standard source-apportionment techniques such as chemical element balance (CEB) could be used.

5. CAN WE DISTINGUISH CRUST, MARINE, AND POLLUTION SOURCES WITHIN THE DEPOSITIONAL COMPONENT?

The three main types of sources for aerosol and deposition are crust, marine, and pollution. They can be found at nearly all locations. In the previous section, we found crustal sources within the depositional component of the lichens. To search for evidence of marine and pollution sources, we need only change the numerator of the horizontal axis to a reference element of that source and search for the appropriate tail at the right end of the plots.

To search for marine components, we used Na/Al on the horizontal axis. Of the four potential marine elements Cl, Br, I, and Mg, only Cl appeared to show a marine component, and it was very weak. Figure 5 shows the marine plot for Cl along with that of Mg, the element likely to have the next-strongest marine signal. Whereas the Cl/Na ratio of the marine tail corresponded well to that of seawater, the analogous tail for Mg fell an order of magnitude above its seawater ratio. Thus Mg in the Portuguese lichens had a main source other than the sea.

To search for a general pollution component (or a coal component) within the deposition, we used Se/Al as the horizontal axis. Plots of all the pollution elements in the lichen data (S, V, Zn, Sb, As, Pb, and even Mn) displayed a pollution tail of unit slope on their right sides. In most plots, the tails were smooth and well-behaved; for V, however, the right end of the tail rose nearly vertically, as though in response to strong specific sources of V. Figure 6 shows the plots for As and V.

The pollution proportions of at least S, Se, V, Zn, Sb, As and Br shown by these plots are essentially indistinguishable from those in European aerosol. Typical proportions were: S/Se = 3000 to 10,000, V/Se = 10 to 40, Zn/Se = 75 to 250, Sb/Se = 0.3 to 1.5, As/Se = 2 to 5, and Br/Se = 30 to 100. Ratios to Se for Pb, for which we have fewer data in aerosol, were 20 to 100. Thus it appears that the pollution elements as a class generally preserve their proportions when deposited to lichens. By contrast, ratios to Se for less-polluted elements such as Mn, Co, and Cr were higher by up to an order of magnitude in lichens than in aerosol, perhaps because of influences from their large crustal components.

6. CAN WE DISTINGUISH SPECIFIC SOURCES WITHIN THE POLLUTION COMPONENT?

6.1. Oil component

The previous section offered preliminary evidence that the lichens showed evidence of a specific oil component. This component can be sought more definitively by placing V/Al on the horizontal axis. These kinds of plots for Ni, the other major element from oil, and Co, an element sometimes found associated with V in aerosol, shown in Figure 7. The plot for Ni is essentially one long oil tail. Its Ni/V ratio of 0.28, as read visually, agrees well with ratios for European aerosol (0.4 to 0.7) and for North American aerosol (about 0.3). The plot for Co is very different. At low Co/Al and V/Al, it shows a broad area of unit slope that is presumably from regionally mixed Co and V in the deposition rather than specific oil sources for Co. At the higher V/Al associated with strong oil signals, Co/Al flattens out and remains constant, further demonstrating that Co in the deposition is not being strongly affected by oil sources. Thus in Portuguese lichens V and Ni but not Co appear to come primarily from oil.

6.2. Incineration component

The prime indicator element for refuse incineration is usually considered to be Zn. Thus we can search for a refuse signal by placing Zn/Al on the horizontal axis. When this is done, Pb and Cl show reasonable tails on the right (Figure 8). These elements are also strongly associated with refuse incineration, Pb from batteries and Cl from PVC. Sb, another element associated with refuse incineration, shows a less-distinct plot than Cl does. On balance, there seemed to be reasonable evidence for a detectable incineration component in the lichens.

6.3. Smelter component

An alternative source for the Pb and Zn might be smelters. With Pb/Al on the horizontal axis, however, Sb, also frequently from nonferrous smelters, failed to show a clear tail. As, even a better smelter element, showed no inclination at all toward a tail. Thus the lichens showed no evidence for a distinct smelter component.

7. HOW DO THESE GRAPHICAL RESULTS COMPARE WITH THOSE FROM FACTOR ANALYSIS?

The other major way to distinguish sources within lichens is factor analysis. Factor analysis has the advantages of being much more established than graphical analysis and of treating all the elements simultaneously. It has the disadvantage of being a black-box technique whose procedure cannot be visualized or easily validated. By contrast, the graphical approach is simple, direct, highly visual, and does not have the problems caused by missing data the way that factor analysis does. Graphical analysis is still being developed, however, is slower and more trial-and-error than factor analysis is, and can deal with only three elements at a time.

7.1. Our general procedure for factor analysis

Our procedure for factor analysis is highly iterative. In general, we use a conventional package such as Statistica to get a quick, basic idea of the solution, and then refine the calculations with the newer PMF2 [5]. We have found that the most important aspects of factor analysis are the choice of elements and the number of factors used. The elements must be of the right type and the right number. Concerning type, elements with poor analytical data or too many points missing (not measured or below detection limit) must be avoided—when too many “bad” elements are included, they create “junk factors” that mean nothing and degrade the other factors as well. It appears to us that the effects of missing data cannot be properly compensated for when more than a very small percentage of the points, possibly as low as 20–25%, are missing. The number of good elements must not be too small, either, or else the results become unstable. The number of factors to retain is very difficult to determine. We seem to be finding that published criteria are often insufficient—we need to examine various numbers of factors for each data set and evaluate their reasonableness based on their stabilities and our experience. We prefer to use the smallest number of factors before nonsensical elements or groups of elements begin to split off.

By contrast, we appear to be finding that while the choice of factor-analysis program is important, it is not so critical as often thought. Once the number of elements has been properly restricted, standard commercial programs perform nearly as well as the larger, research-level programs. For example, we find little difference between Statistica and Positive Matrix Factorization [6]: Whereas PMF2 produces factors with less crossover, Statistica’s remain more stable as their numbers change.

Concerning missing data points, by far the best approach is not to let elements with a significant fraction of missing points into the analysis in the first place. We find that the few missing points for the other elements are best handled by substituting mean values. Lastly, we nearly always use logs of concentrations when dealing with atmospheric data, having found that log-transformed data correspond better to what we see graphically. Although logs of concentrations are less important for bio

TABLE 1. FACTOR SOLUTIONS FOR LOG CONCENTRATIONS, 29 ELEMENTS, AND MEAN SUBSTITUTION

Number of factors	Names	Elements
4	Crust heavy Crust light Lichen Secondary/gas	Na, Al, Si, K, Sc, Ti, Mn, Fe, Co, As, Se, Rb, Cs, La, Ce, Hf, Th, U Sc, Ti, V, Fe, Co, Ni, Sb, I, Pb P, S, K, Zn -Ca, Br, I
5	Crust heavy Crust light Plant Secondary/gas Sea/land	Na, Al, Si, K, Sc, Ti, Mn, Fe, Co, Se, Rb, Cs, La, Ce, Hf, Th, U Sc, Ti, V, Fe, Co, Ni, Sb, Pb P, S, K, Zn S, Br, I Cl, -Ca
6	Crust light Industry/oil Lichen Secondary/gas Land/sea Crust heavy	Al, Si, Sc, Ti, V, Mn, Fe, Co, Ni, La, Ce, Hf V, Ni, Zn, As, Sb, Pb P, K S, Br, I Cl, -Ca Na, Al, Si, K, Rb, Cs, La, Ce, Hf, Th, U
7	Crust heavy Oil/crust light Lichen Secondary/gas Cl/marine Industry Ca	Na, Al, Si, K, Sc, Ti, Mn, Fe, Co, Se, Rb, Cs, La, Ce, Hf, Th, U V, Ni, Zn, As, Sb, Pb P, K S, Br, I Cl Zn, As, Sb, Pb -Ca
8	Crust light Oil Lichen Secondary/gas Cl/marine Crust heavy Ca Industry	Al, Si, Sc, Ti, Mn, Fe, Co, Se, La, Ce, Hf, Th V, Ni, Pb P, K S, Br, I Cl Rb, Cs, La, Ce, Hf, Th, U -Ca As, Sb, Pb
9	Crust light Oil Lichen Secondary/gas Cl/marine Crust heavy Ca Industrial S	Al, Si, Sc, Ti, Mn, Fe, Co, Se, La, Ce, Hf V, Ni P, K Br, I Cl Rb, Cs, La, Ce, Hf, Th, U -Ca As, Sb, Pb S
10	Crust light Oil Lichen Secondary/gas Cl/marine Crust heavy Ca Industry S Mn	Al, Si, Sc, Ti, Fe, Co, Se, La, Ce, Hf, Th V, Ni P, K Br, I Cl Rb, Cs, La, Ce, Th, U Ca As, Sb, Pb S Mn

monitoring data because of the latter's narrow ranges, we chose to use them here for consistency and ease of comparing with our graphical results.

7.2. Iterations

We use iteration to determine whether we should be using logarithmic concentrations, to find the optimal suite of elements, and to find the optimal number of factors. In general, to check the effects of logarithmic versus linear concentrations, we try various combinations of elements and factors

in both modes. To find the optimal suite of elements, we make tables of analytical uncertainties and percent missing data for the elements, start with too many elements, identify the junk factors, and progressively remove the offending elements until all the factors are justifiable. To find the optimal number of factors, we start with too few factors, usually three or four, and progressively increase the number until meaningless single-element factors begin to appear. (Single-element factors can be meaningful, however, if confirmed graphically and environmentally.) Our actual iterative procedure is a compromise that balances all the above the needs. The steps listed below are generally followed separately for logarithmic and linear concentrations.

First, we determine a preliminary list of elements to watch out for by examining the number of data points available for each. For 34 of the 44 elements, 96–100% of the data points were available (Na, Br, Sc, Cr, Co, As, Se, Cs, La, Ce, Sm, Tb, Lu, Hf, Ta, Th, Rb, Eu, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Sr, Hg, Pb, Sb). For another 8 of the elements, between 85% and 91% were available (Nd, W, U, Al, Mg, I, V, Ga). For the two remaining elements, only 58% and 7% were available (Ba, Cd). Taking the first cut at 96% thus tells us to watch out for Nd, W, U, Al, Mg, I, V, Ga, Ba, and Cd. General knowledge of analytical uncertainties of NAA tells us also to be careful for Lu, Hf, Ta, Hg, Eu, Ca, Ni, Cu, and Sb. Beginning with 44 elements, linear concentrations, and four factors eventually yielded six justifiable factors, four junk factors, and 15 problem elements for the ten-factor solution: Mg, Cr, Cu, Ga, Sr, Cd, Ba, Nd, Sm, Eu, Tb, Lu, Ta, W, Hg. Removing these elements and repeating the analysis with 29 elements gave for the preferred eight-factor solution seven defensible factors (crust heavy, oil, lichens, secondary/gas, crust light, sea/land, industry) and only one junk factor (Al and I). Repeating the process with logarithmic concentrations and 44 elements gave seven defensible factors and three single-element junk factors for the ten-factor solution. Removing the same 15 problem elements as before gave eight defensible factors (crust light, oil, lichens, secondary/gas, Cl/marine, crust heavy, Ca, and industry) and no junk factors for the preferred eight-factor solution. Table 1 summarizes the solutions for 4 through 10 factors for the logarithmic case with 29 elements and shows the elements most characteristics of each factor. The eight-factor solution comprised crust light (Al through Hf), oil (V, Ni), lichens (P, K), secondary combustion (Br, I, some S, Se), Cl/marine (Cl, some Na), crust heavy (Rb through U), Ca, and industry (As, Sb, some Pb). All these factors are confirmed graphically, except for possibly the industry or smelter source.

How do the compositions of the factors compare with compositions of the corresponding graphical components? Quite well, it seems, at least for elements in their major sources. To convert factor loadings based on logs of concentrations to masses, one need only multiply together the loading for an element, the exponentiated standard deviation of that element's (logarithmic) concentrations in the lichen samples, and the exponentiated average of the element's (logarithmic) concentrations in the samples. One must be careful, though, to always choose the appropriate factor solution to use for this task. For pollution elements and lichen elements, the eight-factor solution is appropriate, whereas for crustal elements, the three-factor solution is probably best (so as to avoid splitting the crustal factor into heavy and light components). Figures 3 and 7 show two of the better cases, K and V-Ni. For K, I had originally visually estimated the K/Al of its atmospheric component to be about 0.6; factor analysis with three factors subsequently gave 0.45. I had visually estimated the K/P ratio in lichens (the right-hand tail) to be about 3; the eight-factor analysis gave 2.3. On the V-Ni plot, I had estimated the Ni/V ratio in the oil tail to be 0.28; the eight-factor analysis gave 0.28 as well. Thus at least for elements in their major factors, compositions determined graphically and with factor analysis can agree to within 30–40%, and sometimes much better than that. For elements not in their major factors, the situation is less clear-cut and will require careful study.

8. CONCLUSIONS

In brief, this work seems to show that careful graphical analysis of elements in large suites of lichens can distinguish the plant component from the atmospheric component, the soil component from the depositional component within the atmospheric component, the crustal, marine, and pollution components within the depositional component, and at least some types of pollution within the pollution component. Careful factor analysis confirms the plant component, the crustal component but not soil), the marine component, the oil component, the industrial component, and adds a secondary combustion component and a calcium component. These preliminary results are extremely encouraging.

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