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## **Lichen used to assess nickel atmospheric dispersion, an example of New Caledonia**

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**Abstract.** Fifteen epiphytic lichens, collected near an active nickel mine and along an East-West transect across New Caledonia island (South-West Pacific), were analyzed for their metal contents. The purpose is to evaluate atmospheric metal contamination and the impact of mining exploitation on the surroundings. The structure of the compositional dataset was explored using a covariance biplot. The score of the first principal component was used as a generic indicator to locally evaluate the degree of contamination. This study demonstrates that Ni, Co and Cr are highly concentrated in lichens near mining exploitation.

**Keywords:** lichen, nickel, bioindication, compositional data, synthetic indicator

### **1. Introduction**

Atmospheric dispersion of air pollutant is a worldwide problem. Moreover, the increasing number of pollution has peaked over the last decades has implied a more drastic regulation of air pollutants by governments, and the need for relevant monitoring tools of air quality. Lichens have been used as bioindicators of the air quality in various environments ([1]–[3]). Lichens are symbiotic organisms, composed of fungi and algae. They have the ability to accumulate over years metals from the atmosphere. Lichens have no roots, or cuticles and their nutrient uptake therefore relies exclusively on dry or wet deposition, mostly by cation exchange. Bioaccumulation, however, can be influenced by morphological and/or environmental factors, specific to each individual (shape, age, distance from pollution sources, temperature, precipitation or wind direction...).

Nickel is known not only to be released into the environment from natural sources (volcanic emission, forest fire and vegetation,...) but also from anthropogenic activities (fuel combustion, waste disposal incineration, metallurgical activities, mining,...). These later generate small-sized, trace metals enriched, airborne particles which can be spread over a long distance from their sources. They have a deleterious effect on natural ecosystems. On humans, they may extend respiratory dysfunctions, heart diseases, and cancer prevalence ([4]–[6]).

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The dispersion of nickel mining element in an open-pit context is poorly studied. Moreover, mine's access may be problematic in the context of an instrumented monitoring. Lichens could provide therefore an economical and easy set up sampling. In this study, internal metal concentrations of cobalt (Co), chromium (Cr), nickel (Ni), iron (Fe), copper (Cu), zinc (Zn) and titanium (Ti) have been measured in epiphytic lichens collected in and around mining areas. The objective of this study is to assess spatially the impact of these mining areas on atmospheric quality. To fulfil this purpose, we applied statistics especially designed for treating compositional data. A generic index, able to summarize locally the degree of contamination, was drawn from these data and mapped.

## 2. Materials and Methods

### 2.1. Study Area

New Caledonia is a South-West Pacific archipelago, composed of a main island, “Grande Terre”, and three smaller islands (Fig 1 A.). Two thirds of the “Grande Terre” area is composed of weathered ultramafic rocks, forming laterites and saprolites [7]. These rocks, highly enriched in transition metals (Ni, Co, Cr, Mn) form world-class Ni ore deposits which are exploited in wide open-pit mines. An opencast mining, firstly needs the extraction of surface material covering the ore (vegetation and top soil). Secondly, the ore is dug on benches, and then driven down either by 20 t or 30 t truck on unpaved road or by belt conveyor to a loading zone. These mining activities generate dust at each operating step [8], [9].

The present study focuses on the Poro mine, located at the East Coast. It is one of the oldest, still active, mines in New Caledonia.

### 2.2. Sampling

Fifteen lichen thalli were collected in March 2012 from the opencast mine of Poro located at the East Coast and along a transect, towards the West Coast. They were collected on tree trunks, at approximately 1.5 meters above the ground, by means of a plastic knife, and stored in a hermetically plastic bag.

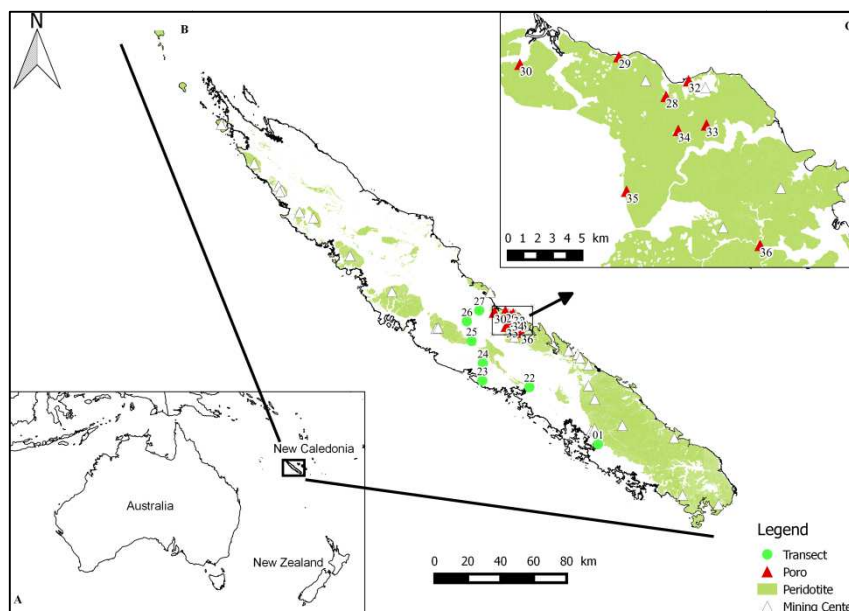


Figure 1: Oceania location of New Caledonia and sampling sites with identification numbers

### 2.3. Analyses of traces elements

At the laboratory, lichens were air dried, removed from bark and crushed in a pre-cleaned agate mortar to obtain a fine powder [1]. Between 20 to 120 mg of powdered lichens were transferred to a beaker with 2 mL each of suprapure HCl, HNO<sub>3</sub> and HF, heated at 105°C, in order to obtain a total dissolution.

Blanks and certified reference materials (CRMs), namely peach leaves (NIST 1547), lichens (BCR-482), and basalt (BCR2), were processed together with each batch of unknown samples. Solutions, appropriately

diluted with Milli-Q water, were analysed for Co, Cr, Ni, Fe, Cu, Zn and Ti, using an Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-AES) Spectro Arcos.

The limits of detection (LOD) were calculated on the basis of three times the standard deviation of five analytical blanks. Differences between measured and certified concentrations may reach 30% at worst (Table 1). It is not however, a crippling drawback because the concentration's dynamic observed within the set of samples is quite huge. A blank correction was nonetheless applied to raw sample concentrations, although it accounted for less than 10% for all elements.

	Co	Cr	Cu	Fe	Ni	Zn	Ti
<b>LOD (µg/g)</b>	0.19	0.19	0.98	2.12	0.21	0.08	0.55
<b>BCR 2 (µg/g)</b>							
<b>Measured</b>	45	11	20	5.9 <sup>b</sup>	8	98	1.2 <sup>b</sup>
<b>Certified</b>	37	18	19 <sup>a</sup>	9.6 <sup>b</sup>	-	127	1.3 <sup>b</sup>
<b>BCR 482 (µg/g)</b>							
<b>Measured</b>	0.47	3.25	6.20	701	2.31	87	78.2
<b>Certified</b>	0.32 <sup>a</sup>	4.12	7.03	804 <sup>a</sup>	2.47	100.6	-
<b>NIST 1547 (µg/g)</b>							
<b>Measured</b>	nm	1.0	2.6	185	0.76	17.4	23
<b>Certified</b>	0.07 <sup>a</sup>	1.0 <sup>a</sup>	3.7	218	0.69	17.9	-

Table 1: Quality control of the analyses. nm for below detection limits; - to the best of our knowledge, no data available; <sup>a</sup> provided but not certified; <sup>b</sup> expressed in per cent

### 3. Results and discussion

The highest concentrations in Cu and Ti were observed in lichens collected from transect sites (21 µg/g and 478 µg/g, respectively), while the highest concentrations in Ni, Co, Cr, Fe and Zn (5216 µg/g, 323 µg/g, 1612 µg/g, 6.68 % and 147 µg/g, respectively) were measured near Poro mine (Table 2).

Sample ID	Section	Co	Cu	Cr	Fe	Ni	Zn	Ti
1	Transect	2.1	8.2	26	0.19	42	74	128
22		3.4	0.82	19	0.53	31	76	470
23		2.1	1.4	22	0.19	28	77	163
24		6.6	21.	30	0.75	59	20	478
25		3.2	nm	28	0.23	54	88	172
26		5	6.4	57	0.37	51	22	347
27		0.85	nm	13	0.10	20	19	72
28	Poro	175	2.4	1612	6.68	3535	147	64
29		13	0.47	111	0.53	204	32	9.5
30		24	5.4	254	1.37	391	36	164
32		323	13	1503	6.15	5216	75	68
33		10	5.5	666	1.84	324	29	43
34		0.31	0.70	11	0.04	12	3.5	2.7
35		10	0.76	118	0.48	191	48	27
36		63	12	564	2.02	948	44	27

Table 2: Trace element concentrations (in µg/g, except iron content in %w/w) for all lichens. nm: below LOD

It is common to normalize trace element's amount measured in lichens by concentrations of a crustal origin element [1], [10] to overcome individual variability related to exposure, age, etc. of each lichen. However, pair ratios containing a common and variable denominator can lead to spurious correlations [11]. To avoid this problem, a compositional data analysis is highly recommended ([12], [13]).

Compositional data consists of vector  $\mathbf{x} = [x_1, x_2, \dots, x_D]$ , for  $D$  trace metal concentrations, satisfying a sum constraint less than or equal to 1. The compositional dataset is first centred log ratio (*clr*)-transformed to avoid such spurious correlations [14]:

$$\text{clr}(\mathbf{x}) = \left[ \ln \frac{x_1}{g_m(\mathbf{x})}, \ln \frac{x_2}{g_m(\mathbf{x})}, \dots, \ln \frac{x_D}{g_m(\mathbf{x})} \right]$$

where  $g_m(\mathbf{x})$  corresponds to the geometric mean of  $g_m(\mathbf{x}) = (x_1 \cdot x_2 \dots x_D)^{1/D}$ . Then, the covariance biplot can be computed from this new compositional dataset (Figure 2), where log-ratios of the variables (trace metals) and sites (lichen samples) can be represented on a same diagram.

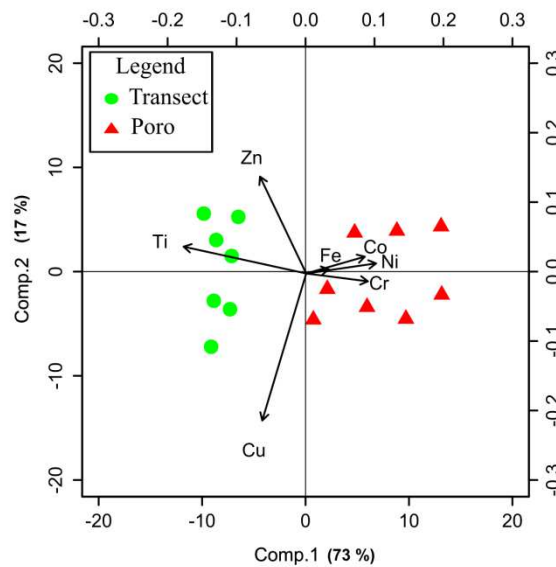


Figure 2: Compositional covariance biplot for lichens projected on the first two principal components

At that point, it should be recalled that the interpretation of a compositional covariance biplot is somehow different from that of a traditional biplot. The line connecting two variables arrow heads, namely a link, represents the log-ratio between the two involved variables, and the length of this link indicates the variation of these log-ratio (or ratio). The angle between two links estimates the correlation between log-ratio (a linear link or with an angle near  $0^\circ/180^\circ$  indicates that log-ratios are correlated) [14].

In our case, the first and second components explain 73% and 17%, respectively, of the total variance (sum= 90%, cf Figure 2). Figure 3 shows the impact of variables on principal components. When bars are above or below the line equal to 1, the variables have an influence on the component. It appears that component 1 is highly influenced by Co/Ti, Cr/Ti, Fe/Ti and Ni/Ti log-ratio variables, whereas component 2 is influenced by Co/Cu, Cr/Cu, Fe/Cu, Ni/Cu and Zn/Cu log-ratio variables. Interestingly, the short links between mining elements (i.e. Co, Cr, Fe and Ni) indicate subcompositions of low variance (Figure 2).

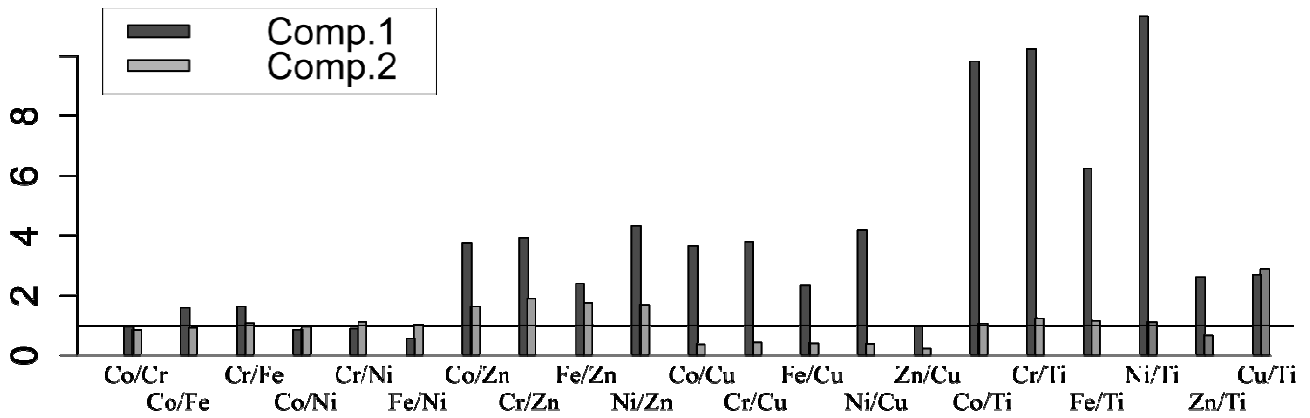


Figure 3: Bar plots of loadings of a compositional principal component analysis

The Poro lichens, which exhibit the highest concentrations of elements possessing a mining origin (Co, Ni, Cr, and Fe) always plot in the right part of the diagram (i.e. the positive part of component 1), whereas those originating from the transect, plot in the left part. Such visually observable difference is easily confirmed by a multivariate analysis of variance ( $p < 0.01$ ). However, MANOVA is unrealizable on the *clr*-transformed data because the covariance matrix is singular. To overcome this singularity, an isometric log-ratio (*ilr*-)transformation is applied [15]:

$$ilr(x) = z = [z_1, \dots, z_{D-1}] \in \mathbb{R}^{D-1}; z_i = \sqrt{\frac{i}{i+1}} \ln \sqrt{\frac{\prod_{j=1}^i x_j}{x_{i+1}}} \text{ for } i=1, \dots, D-1$$

To determine the degree of pollution, several multi-element indices have already been constructed ([16], [17], [18]), using, for instance, the mean concentration or a combination of 10th percentiles of each element. Meyers et al [12] have recently shown that score of a compositional biplot can be used as an efficient synthetic indicator of pollution (Meyer's Indice). In the present case, the scores of PC1 are extremely well-adapted to such a purpose, as discussed above.

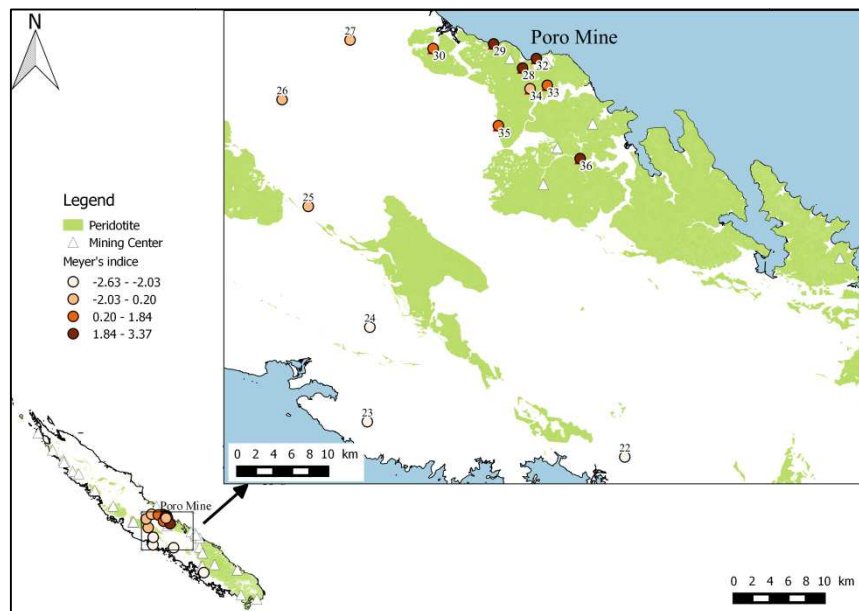


Figure 4: Synthetic indicator of lichen contamination

As expected, the Meyer's synthetic indicator demonstrates that Poro mine region is more impacted than locations belonging to the transect (Figure 4). The influence of mining activities is observed up to 30 km away.

## 4. Conclusion

Air monitoring by lichens has proved to be very effective to evaluate nickel-contaminated environments. The presence of mining activities in New-Caledonia leads to increased incorporation of Ni, Co, Cr by these organisms. The use of adapted compositional data analysis allows a synthetic index of pollution to be computed on the basis of first principal component. This index can also be mapped to estimate the dispersion of metal from the mining area. Such data can be used to improve the management of impacted areas and to better protect the ecosystems in the future. Further studies are required to evaluate atmospheric depositions over a wider area and other contaminated sites (smelters, abandoned mines, etc...), and their ecotoxicological impacts.

## 5. Acknowledgements

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