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ENRICHMENT FACTORS OF ELEMENTS IN LICHENS FROM THE MACHU PICCHU ANTARCTIC SCIENTIFIC STATION (2013)

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1. Introduction

To evaluate properly the extent of accumulation and movement of toxic substances in the environment there must be reliable of their present and past concentrations. The purpose of one project at the IPEN Antarctic Program is to determine the recent depositional history of trace elements associated with energy production in lichens of Mackellar Inlet. Elements which are toxic, potentially toxic or may have deleterious effects on biota were selected for analyses.

The study of the accumulation or metal enrichment in soil is based on normalization of geochemistry techniques, which allow knowing the index of geo-accumulation and enrichment factors (EF). The EF reports the dynamics of a chemical element or inorganic contaminant of the Earth's crust that can be transported by rain, wind or anthropogenic sources (Hansen *et al*., 1995; Reiman and Caritat, 2000).

The enrichment factor(EF) has been used in studies of eco-toxicology and environmental chemistry as a reference. Consider the most abundant elements in Earth's crust such as Al, Si and Fe (Lawson and Winchester,1979; Poissantetal,1994; Stiotyketal, 2002).The enrichment factor may be interpreted as follow: If an element exists in its crustal ratio, EF = 1, then it may assumed that the main source of the element is the earth´s crust. Any rations other than EF=1 are assumed to be due to local variability. For example if the ratio is EF > 1, additional sources of input besides geological release are indicated while EF < 1 may be interpreted as an indication of local depletion in a particular element (Heit*et al*., 1980; Krauskopf, 1967).

The aim of this study is to determine the EF of certain elements that can be used as tools for environmental impact assessment in the region due to anthropogenic activities

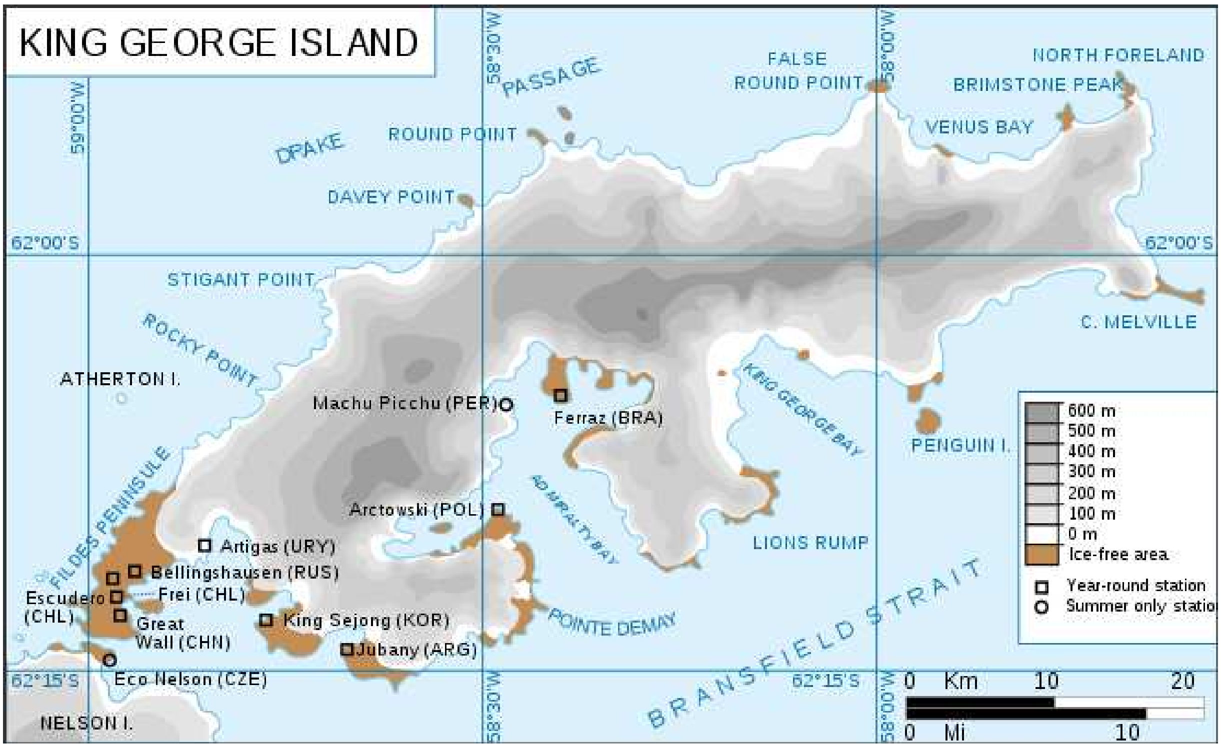
2. Material and Methods

The Machu Picchu Antarctic Scientific Station (Figure No.1) is a Peruvian polar scientific research facility in Antarctica, established to conduct Antarctic research on geology, climatology and biology. More specifically, its purpose is to study the continent's geological past, potential sea resources, wind strengths, air pollution, and the animal adaptation in a freezing environment.

Source: Ángel Ramírez (UNMSM)

Figure No.1: Machu Picchu Antarctic Scientific Station

Mackellar Inlet **(**Coordinates: 62°5′S 58°28′W) is an inlet forming the northwestern head of Admiralty Bay, at King George Island in the South Shetland Islands (Figure No. 2). It was probably named by the Fourth French Antarctic Expedition under Jean-Baptiste Charcot, who charted Admiralty Bay in December 1909.Admiralty Bay is an irregular bay, 8 km (5 mi) wide at its entrance between Demay Point and Martins Head, indenting the southern coast of King George Island for 16 km (10 mi), in the South Shetland Islands of Antarctica. The name appears on a map of 1822 by Captain George Powell, a British sailor, and is now established in international usage. It has been designated an Antarctic Specially Managed Area (ASMA 1).



Source: Wikipedia

Figure No.2: Location of Machu Picchu Antarctic Scientific Station

Lichen and soil samples were collected from Mackellar Inlet, near the Peruvian Antarctic Station, at Admiralty Bay, during the 2012/2013 Austral summer (Table No.1), lichen samples were identified as *Usnea antarctica* Du Rietz (Mckenzie, 1964).

The sample collection and identification was carried out by a biologist-lichenologist of the Natural History Museum of the Universidad Nacional Mayor de San Marcos (UNMSM) from Lima, Peru.

Table No.1: Sampling of Lichen and Soil form Mackellar Inlet

Sample	Code	Geographical Location		Altitude	Date
		Latitude	Longitude	(m)	
Lichen	L1	62,09344444° S	58,4692500° W	21.00	2013-02-19
	L2	62,09427778° S	58,4738056° W	30.00	2013-02-19
	L3	62,09185700° S	58,4756810° W	3.00	2013-02-22
Soil	S1	62,09411000° S	58,4674300° W	6.37	2013-02-20
	S2	62,09359000° S	58,4697100° W	21.00	2013-02-20
	S3	62,09191000° S	58,4763300° W	8.00	2013-02-21
	S4	62,09282200° S	58,4687650° W	5.00	2013-02-22

Source: Ángel Ramírez (UNMSM)

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Figure No.3: Sampling of Surface Soil

The multi-element quantitative analyses of the samples were performed by the Division of Nuclear Analytical Techniques, of Instituto Peruano de Energía Nuclear (IPEN) by neutron activation analyses (Montoya *et al*., 2010).The concentrations of elements are expressed at a level of 95% uncertainty and the results were statistically evaluated by analysis of variance with 95% confidence, in order to determine the existence of differences between sampling areas.

The enrichment factor model is represented as:

$$EF = \frac{\left(\frac{X}{Al}\right)_{Lichen}}{\left(\frac{X}{Al}\right)_{crust}}$$

Where X is the concentration of the element of interest in the sample and in the earth´s crust, and Al is the concentration of Al in the sample and in the earth´s crust.

3. Results and Discussion

As shown in Table No.2 and Figure No.4, Al, Ca, Fe, K and Mg appear in higher concentrations in lichen samples with respect to the other elements analyzed. While K, Ca, Fe, Zn, Mg and Mg are typical bio-elements, is interesting the high concentration of aluminum present in these organisms

Table No.2: Average Element Concentrations in Lichen (µg/g dry weight)

Element	L1	L2	L3
Al*	0,260 ± 0,010	0,160 ± 0,010	0,100 ± 0,005
As	0,740 ± 0,050	0,500 ± 0,030	0,590 ± 0,030
Au	0,006 ± 0,001	0,003 ± 0,001	0,004 ± 0,001
Ca*	0,600 ± 0,040	0,700 ± 0,040	1,400 ± 0,080
Co	0,800 ± 0,040	0,350 ± 0,020	0,330 ± 0,020
Cr	1,200 ± 0,100	0,560 ± 0,030	0,300 ± 0.020
Cs	0,110 ± 0,010	0,086 ± 0,005	0,063 ± 0,004
Fe*	0,240 ± 0,014	0,140 ± 0,010	0,100 ± 0,010
K*	0,200 ± 0,030	0,200 ± 0,010	0,200 ± 0,030
Mg*	0,100 ± 0,011	0,475 ± 0,026	0,100 ± 0,010
Mn	36,000 ± 2,000	19,000 ± 1,000	36,000 ± 2,000
Se	2,000 ± 0,220	1,700 ± 0,090	1,600 ± 0,100
Zn	11,200 ± 0,650	5,600 ± 0,300	18,600 ± 1,000

(*): µg/g x 10^4

Source: Division of Nuclear Analytical Techniques (IPEN)

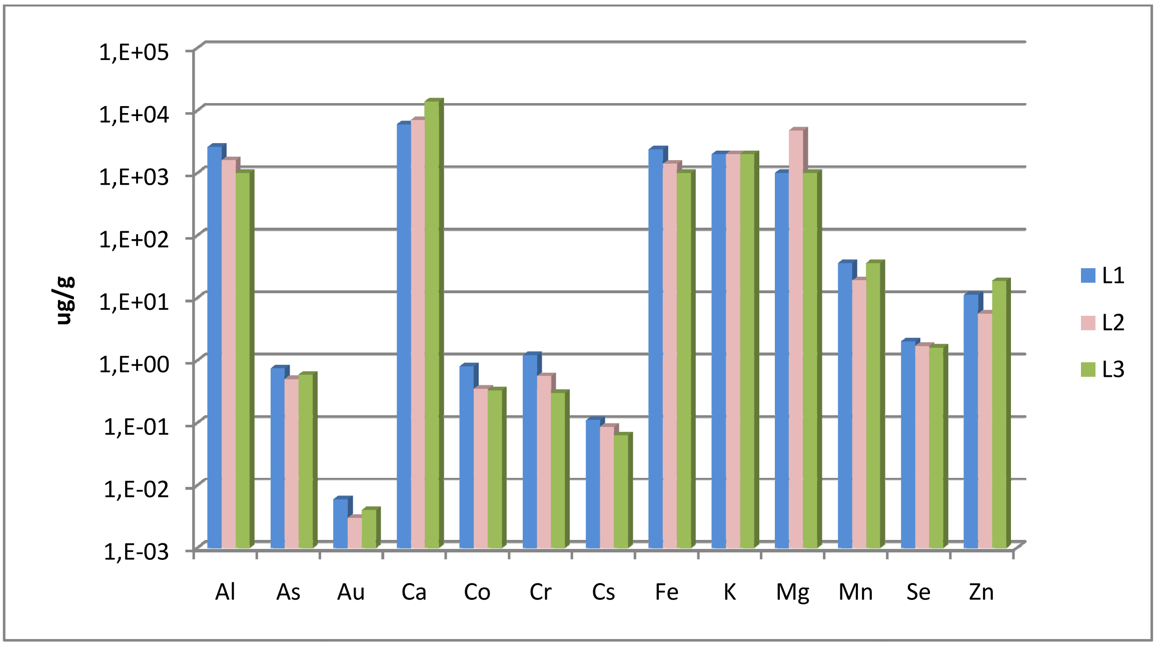

Figure No.4: Average Element Concentrations in Lichen (µg/g dry weight)

The analysis of variance in lichen for different sampling areas showed no statistical differences at 95% confidence (Table No.3); based on these results it can be stated that the distribution of these elements in the atmosphere is homogeneous.

Table No.3: Analysis of variance from Lichen Results

Sources	Degree of Freedom	Sums of Squares	Mean Squares	F value	F critical
Sampling areas	2	966179.2763	483089.6381	0.23780062	3.402826105
Elements	12	223070001.2	18589166.76	9.15050754	2.183380082
Error	24	48755765.78	2031490.241		

As shown in Table No.4 and Figure No.5, the presence of typical elements of the earth's crust such as Al, Fe, K and Ca is verified.

Table No.4: Average Element Concentrations in Soil (µg/g dry weight)

Element	S1	S2	S3	S4
Al*	7,100 ± 0,400	7,300 ± 0,400	7,600 ± 0,400	7,700 ± 0,450
As	20,000 ± 1,200	19,000 ± 1,000	12,600 ± 1,000	13,000 ± 1,000
Au	0,031 ± 0,002	0,035 ± 0,002	< 0,025	< 0,025
Ca*	1,600 ± 0,100	1,500 ± 0,100	2,800 ± 0,160	2,100 ± 0,130
Co	14,000 ± 1,000	11,000 ± 0,600	16,000 ± 1,000	12,500 ± 1,000
Cr	19,000 ± 1,100	22,000 ± 1,300	34,1000 ± 1,900	18,000 ± 1,000
Cs	2,000 ± 0,100	2,600 ± 0,100	1,700 ± 0,100	2,000 ± 0,100
Fe*	5,200 ± 0,300	5,800 ± 0,300	6,900 ± 0,400	5,000 ± 0,300
K*	1,600 ± 0,100	1,700 ± 0,100	1,200 ± 0,100	1,400 ± 0,100
Mg*	1,140 ± 0,100	1,120 ± 0,100	1,600 ± 0,100	1,200 ± 0,100
Mn*	0,630 ± 0,036	0,650 ± 0,038	1,000 ± 0,060	0,740 ± 0,043
Se	9,000 ± 0,500	9,000 ± 0,500	3,400 ± 0,200	4,000 ± 0,200

(*):µg/g x 10^4

Source: Division of Nuclear Analytical Techniques (IPEN)

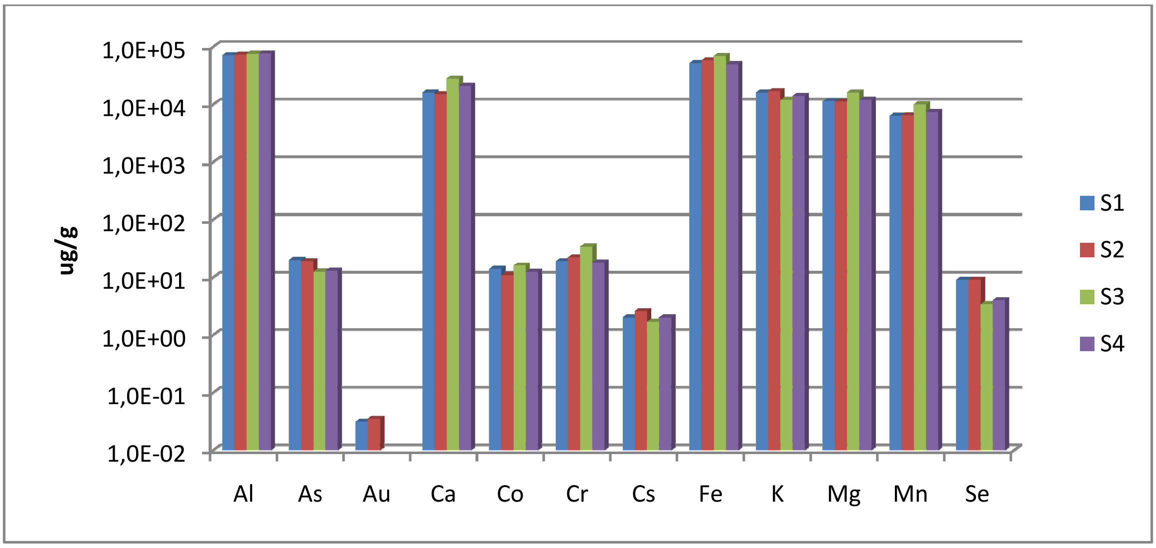

Figure No.5: Average Element Concentrations in Soil (µg/g dry weight)

Moreover, analysis of variance in different areas soil sampling showed no statistical differences at 5% confidence (Table No.5), so it is assumed that the distribution of the elements is uniform in soil crust

Table No.5: Analysis of variance from Soil Results

Sources	Degree of Freedom	Sums of Squares	Mean Squares	F value	F critical
Sampling areas	3	77333438.55	25777812.85	2.503374209	2.922277191
Elements	10	25851240631	2585124063	251.050504	2.164579917
Error	30	308916814.2	10297227.14		

The enrichment factors (EF) for each element of interest are given in Table No.6. The elements Ca, K, Mg and Se appear to be significantly enriched throughout the core with EF > 5. Other elements, except Mn, also appear to be enriched although to a lesser extent.

Table No.6: Enrichment Factors (EF) for each element of interest in Lichen Samples

Element	L1	L2	L3
Al*	1.00	1.00	1.00
As	1.31	1.44	2.71
Au	5.19	4.22	9.00
Ca	8.57	16.24	51.98
Co	1.71	1.21	1.83
Cr	1.47	1.12	0.96
Cs	1.51	1.92	2.25
Fe	1.20	1.13	1.30
K	3.87	6.29	10.07
Mg	2.26	17.43	5.87
Mn	0.14	0.12	0.35
Se	8.99	12.42	18.71

(*) The Al enrichment factor is 1.00 by definition

According to the classification of Lawson and Winchester (1979), the majority of elements showed to a value EF less than 10, so that its presence in soil is due to the bedrock (Table No.7). The high values found in K and Ca for some samples may be due to the contribution of remains of marine and continental organisms. In the case of selenium, it will be necessary to further study to identify the source of its enrichment

Table No.7: Enrichment Factors Classification

FE	Origin of the Element
1 – 10	From Earth´s crust
10 – 500	Moderately enriched and indicates other sources of additional enrichment bedrock
>500	High enrichment and shows that there is significant contamination of anthropogenic origin

Source: Lawson and Winchester (1979)

4. Conclusion

The results obtained in this study shows that the environment has not been contaminated by the activities carried out in the Machu Picchu Antarctic Scientific Station. However, it is important to note that further studies are needed on the concentrations of other elements such as lead, mercury and hydrocarbons to confirm the impact of human activities in this region.

5. Acknowledgments

Our thanks to the biologist-lichenologist Ángel Ramírez, from the Natural History Museum of the Universidad Nacional Mayor de San Marcos, Floristic Lab, Department of Dicotyledons, for their support in the identification and collection of specimens of *Usnea antarctica* Du Rietz, under the authorization of the MRE 001-2013. We also acknowledge to Patricia Bedregal and Pablo Mendoza from the Division of Nuclear Analytical Techniques, of Instituto Peruano de Energía Nuclear, for their aid with the analysis of samples.

6. References

Hansen, A. H.; Z. A. León e I. L. Bravo (1995). "Fuentes de contaminación y enriquecimiento de metales en sedimento de la cuenca Lerma-Chapala", *Ingeniería Hidráulica en México*, 3: 55-59.

Heit M., Klusek C., Volchok H., Burke J. (1980) ¨The Concentrations of Eighteen Trace Elements in a Dated Sediment Core from Standley Lake, CO¨ Environmental Quarterly. Environmental Measurements Laboratory.U.S. Department of Energy.EML-371.UC-11. December-March 1980: I-72,74.

Krauskopf KB. (1967) ¨Introduction to Geochemistry¨, McGraw-Hill. New York, NY., pp. 638-640.

Lawson, D. R. y J. W. Winchester (1979). "A Standar Crustal Aerosol as a Reference for Elemental Enrichment Factors", *Atmospheric Environment*.10: 925-930.

Mckenzie D. (1964) ¨Antarctic Lichens. I The Genera *Usnea, Ramalina, Himantormia, Alectoria, Cornicularia*¨. British Antarctic Survey. Scientific Reports No.38. London. Pages 5-8.

Montoya E., Bedregal P., Mendoza P., Ubilluz P., Torres B., Cohen IM (2010).¨The developmentofthe k_0 method inPeru:Past,presentand future perspectives¨.Nuclear Instruments and Methods in Physics Research A 622: 381–384

Poissant L.; J. P. Schmitt y P. Béron (1994). "Trace Inorganic Elements in Rainfall in the Montreal Island", *Pergamon Press*. England.

Reiman, C. y P. de Caritat (2000). "Intrinsic Flaws of Element Enrichmentes Factors (EFs) in Environmental Geochemistry", *Environmental Science & Technology*. H.W. Wilson-AST; 34 : 5084-5091.

Stiotyk, W.; D. Weis y M. Hesterkamp (2002)."New Peat Record of Atmospheric Lead Pollution in Switzerland: Pb Concentrations EnrichmentFactors, Isotopic Composition, and Organolead Species", *Envionmental Science & Technology*, 36: 3893-3900.