Global Journal of Human-Social Science: B
Geography, Geo-Sciences, Environmental Science & Disaster Management
Volume 22 Issue 4 Version 1.0 Year 2022
Type: Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals
Online ISSN: 2249-460X & Print ISSN: 0975-587X

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GJHSS-B Classification: DDC Code: 338.479172981 LCC Code: G155.C35

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Student t-test for the comparism of the halogens with regards to the substrate (Table 4) shows no significance difference in the means of the all the halogens but a slight difference (p= 0.048 at 0.05 levels) in the variance of Cl. The box-plot (fig 3) also confirms the slight difference in Cl. *Leptogium gelatinosum* was identified as the highest sequesters, followed by *Heterodermia obculata* and least was *Parmotrem atinctorum*. Fluorine was the most dominant halogen with concentrations ranging from 0-188 µg/g with mean values of 78 ± 49 and bromine the least. The concentrations were higher for specimens located close to the coastal areas in the downwind direction compared to those found further inland.

Keywords: lichens, mount cameroon, leptogium gelatinosum, fluorine and halogens.

I. INTRODUCTION

Volcanic regions have always attracted many people worldwide because of the high fertility of their soils (Diana *et al.,* 2019). However, human proximity to volcanoes can lead to several health problems as consequence of the chronic exposure to the materials released from the volcanic activity. An element often found in elevated concentrations in volcanic regions is fluorine. Although fluoride is recognized to have a beneficial effect on the rate of occurrence of dental caries when ingested in small amounts, its excessive intake results in a widespread but preventable pathological disease called fluorosis (Dey and Giri, 2015) While skeletal fluorosis, the most severe form of fluorosis, requires a chronic exposure to high concentrations of fluoride in water (4–8 mg/L), dental fluorosis occurs after shorter periods of exposure to fluoride in lower concentrations (1.5–2.0 mg/L). In some volcanic regions, where exposure to elevated amounts of fluoride is persistent, biomonitoring programs are fundamental (Garcia and Borgnino, 2015).

In the present world pollution scenario, a comprehensive knowledge of pollutants and their adverse effects on the ecosystem are required for selection of a workable monitoring and conservation technique (Munzi *et al.,* 2012; Ahmad *et al.,* 2007). The increasing awareness of the potential hazards and impact of air pollution on the health of human populations, forest decline, climate change and loss of agricultural productivity, for example, has been a cause of increasing public concern throughout the world (Smodis, 2007). This has highlighted the need for continuous monitoring of the levels of pollutants in the environment (Garty *et al.,* 2002). Environmental monitoring approaches that are cheap, can be used anywhere, and respond to many kinds of airborne pollutants are needed to fingerprint the pollutant sources and their dispersion pattern (Larsen *et al.,* 2007). A comprehensive approach to reduce the impacts of pollution and climate change, an approach that decreases emissions across all sectors and enhances the adaptive capacity of all nations with economic reflections is needed (Pinhoa *et al.,* 2012).

Lichens emerge as the key answer to this monitoring problem and are the flora of choice for monitoring studies (Notcutt and Davis, 1989). They obtain their nutrients directly from the atmosphere and their chemical composition therefore holds the promise of becoming a natural or 'green' technique for monitoring the health of the environment around passively degassing volcanoes and industries. Bio-accumulation in lichen thalli has been used as a major tool for assessing air quality in volcanic and industrial areas (Bennett, 2006). They are extremely valuable in environmental monitoring since they exist worldwide and

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are sensitive to many different kinds of pollutants (Brodeková *et al.,* 2006). They are slow growing; do not shed parts and are perennial pioneer plants commonly described as sentinel organisms (Loppi *et al*., 2002). They are good bio-accumulators of heavy metals and trace elements and can be transplanted where they do not occur in nature (Llop *et al.,* 2012).

Lichens are mutual symbiosis between fungi with an algal and/or a cyanobacterial partner (Morris and Purvis, 2007). The success in lichenization is attributed to a genetic combination resulting from metabolic biomolecules and influenced by environmental factors (Jatinder *et al.,* 2012). This process has created unique characteristics in lichens such as the unique anatomical (absence of roots, stomata, vascular tissues and cuticle) and physiological (poikilohydry and absorbance of nutrient from general thallus surface from the atmosphere. These peculiarities, allow lichens to grow in all sorts of terrestrial habitats comprising 8% of vegetation.

According to Lawrey (1986), lichens produce a wide array of more than 1000 unique secondary metabolites (depsides, depsidones, β-orcinoldibenzyl esters, and xanthones, usnic acid and pulvinic acid derivatives, for example) as adaptations for life in marginal habitats. These secondary metabolites assist to maintain the lichen symbiotic association and compete with organisms sharing the same niche (Culberson and Culberson, 2001). Another characteristic stress-resistance mechanism is the accumulation of melanin and oxalate crystals in their thallus, which provide a crystal layer on the thallial surface making lichens tolerant to extreme environments and good bio-accumulators of atmospheric substances (Hess *et al.,* 2008). Most lichens are tolerant to high concentrations of atmospheric pollutants well beyond levels necessary for their physiological requirement by sequestrating and accumulating varied oxalate crystals (Garty *et al.,* 2002; Bjerke *et al.,* 2002; Chen *et al.,* 2000). The aggregates of these oxalate crystals disintegrate and provide a crystal layer on the thallial surface making lichens good bio-accumulators. Since lichens do not shed parts (Walker *et al.,* 2003; Monge-Nájera *et al.,* 2002), and bio-accumulate pollutants safely in their thalli over time, pollutants levels can be professionally determined quantitatively by chemical analysis of species and qualitatively by observing species diversity, abundance and distribution (Jovans, 2008). With their indiscriminate ability to absorb and bio-accumulate both nutrients/ pollutants from the atmosphere, elevated concentrations of certain elements in lichens are a sure sign of atmospheric deposition (van Herk, 1999).

Lichens can be used as bio-monitors of pollutants by quantifying the amount of trace element(s) accumulated within them over time (Srivastava *et al*., 2015, Bargagli, 2016). They have been used to assess deposition and air quality in hundreds of studies worldwide (Donahue, 2018). Ayrault *et al.,* 2007, have shown a relationship between the quantities of pollutants in the environment and those concentrated in lichen thallus. A variety of elements and chemical compounds affecting lichen growth and distribution are found in the atmosphere (Bajpai *et al*. 2011). Pollutants, including sulfur dioxide (SO_2), nitrogen dioxide (NO_2) and fluoride (F) compounds, remain in the same chemical form after they are emitted into the atmosphere and are easily absorbed by lichens. Gases like chlorine and fluorine, leads to the injury of fundamental metabolic processes, which arise by acidifying the water and the substrates, resulting in the loss of most sensitive lichen species (Brodeková *et al.,* 2006). Many lichens are sensitive to fluorine pollutant as it can concentrate in hydrated lichens to more than 200 times ambient concentrations (Notcutt and Davis, 1989). Fluoride are highly toxic to lichens, and elevated levels of fluoride are correlated with chlorophyll breakdown, reduced ATP concentration, reduced photosynthesis and disappearance of species (Stefano and Luisa, 2006). In general, obvious damage to lichens begins at levels of 50-70 ppm.

In most parts of Europe like Germany for example, (Hauck, 2005), lichen transplants from pristine to polluted areas are carried out to bio-accumulate atmospheric pollutants. The lichen *Hypogimnia physodes* was used to bio-accumulate radionuclide Uranium (Golubev *et al.,* 2006) and rare earth elements in Czech Republic (Jitka *et al.,* 2010). The fruticose lichen *Stereocaulon vesuvianum*, growing on the slopes of Mount Vesuvius in South Italy, was used as a bio-monitor of ^{134}Cs, ^{137}Cs, ^{103}Ru and ^{106}Ru derived from the April 26, 1986 Chernobyl nuclear reactor disaster (Environment Canada, 2003). Grasso *et al.* (1999) found that lichen composition reflects the contribution of the volcanic activity in Mount Etna and Vulcano Island. They noted that, distribution of the degassing elements (arsenic (As), antimony (Sb), Br, and lead.

Volcanoes emit a variety of gases both between and during eruptions, including H_2O, CO_2, SO_2, HCl, NH_3, H_2S, HF and a few other minor constituents (Cronin and Sharp, 2002). These gases interact rapidly with the ash particles of a volcanic plume and especially atmospheric water to form acidic aerosols. These aerosols given off during and after volcanic eruptions caused problems on a number of occasions when it has accumulated in low lying areas. Exposure to excessive amounts of fluoride may cause adverse health effects for humans and animals (Conti *et al*., 2016) The plume dispersed by winds after a volcanic eruption contains volcanic ash that may also be a source of fluoride at levels that are potentially toxic. Fluorides are released into the environment naturally through the weathering and dissolution of minerals, the emissions from volcanoes and from marine aerosols (WHO, 2002) fluoride emissions from volcanoes and the natural occurrence of excessive amounts of fluoride in drinking water have affected the health of humans and livestock for centuries, if not millennia. Although sometimes of anthropogenic origin, high levels of fluorine are generally related to natural sources. Volcanic emissions of fluorine take the form of either sluggish permanent release from quiescent volcanoes (passive degassing) or rarer but more impacting discharges during short-lived volcanic eruptions (Schwandner *et al.,* 2004 Linhares *et al.,* 2017). It has been estimated that passive degassing, like that existing at Mt. Etna (Italy) and Masaya (Nicaragua) volcanoes, accounts for about 90% of the volcanic fluorine release. The influence of these emissions on the surrounding environment and in particular on vegetation has been investigated by several authors (Nelson and Wheeler, 2016).

Little or no bio-accumulation and monitoring work have been carried out on the active Mt. Cameroon. Mount Cameroon volcano with a return period of 20 years (Suh *et al.,* 2003), has been the most frequent erupted volcano in West Africa, with eight eruptions in the last 100 years (1909, 1922, 1925, 1954, 1959, 1982, 1999 and 2000). It constantly releases various constituents into the environment during active eruptions and even in quiescent degassing periods (Suh *et al.,* 2008). These researchers reported that, Mt. Cameroon basanites melt inclusions has shown high levels of carbon dioxide with a concentration of 967 µg/g, sulphur 2400 µg/g, chlorine 1270 µg/g and fluorine 1530 µg/g. In spite of these findings, there is little knowledge of lichens toxic levels and remediation of the high levels of halides release from this volcano.

The objective of this paper was to determine the concentration levels of some halogens and identify potential lichens species that can be used as appropriate bio-accumulators of halide toxicity for Mt. Cameroon degassing volcano.

II. Materials and Methods

a) Description of the Study Area

i. *Location*

The study area (Fig.1) is the active MC volcano located in the coastal belt of the Gulf of Guinea, South West Region of Cameroon. It lies between Latitudes 3°57’ to 4° 27’N and Longitudes 8° 58’ to 9° 24’E (Suh *et al.,* 2003). It is the highest peak in West Africa, is of volcanic origin and rises from the Atlantic Ocean to a height of 4100 m. It covers a surface area of about 1750 km^2 (DeLancey and Mark, 2000).

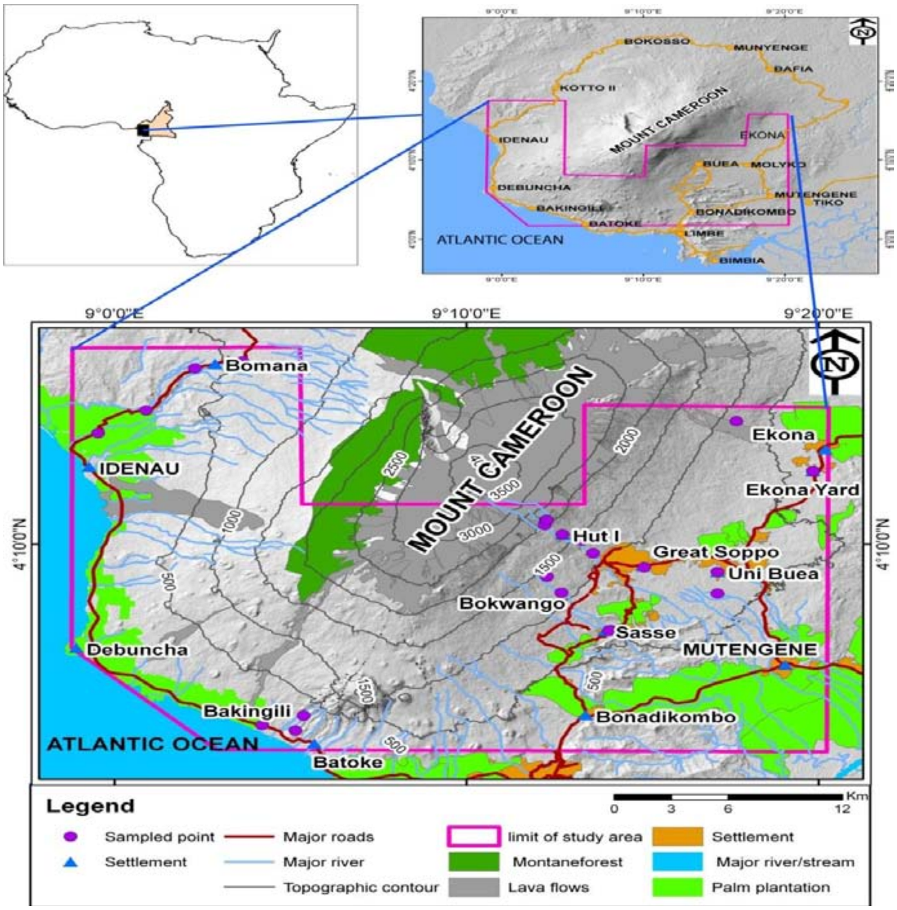

Fig. 1: Topographic features of Mt. Cameroon and location of sampling sites mentioned in the text.

b) *Sample Sites*

The survey sites were divided into Northern and Southern contrasting flanks following wind direction and ash fall trends from various eruptions. The northern flank was called the leeward and southern flank was called the windward. Out of the eight sites selected on the two flanks, four were on the leeward flank (Lower Buea, Upper Buea, IRAD-Ekona and Ekona-Mbenge) and four from the windward flank (Batoke, Bakingili, Idenau and Bomana). Lower Buea on the leeward flank comprises of University of Buea campus, Great Soppo, and Sasse. Some species were collected from control area of Mamfe (5.7512° N – 9.3146° E) about 270 km from Mt. Cameroon.

The survey was also done based on altitudinal levels which ranged between 3 to 2178 m above sea level (Table 1). The altitudinal levels were divided into three (low, mid and high) ranges.

Table 1: Altitudinal ranges of sampling sites.

Altitude	Range(m)	Sites
Low	3 -499	IRAD-Ekona Batoke Bakingili Idenau
Mid	500-1000	Ekona-Mbenge Lower Buea Bomana
High	>1000	Upper Buea

c) *Sample Selection*

Thirty-four macro lichens (Foliose and Fruticose) species from six families, eight genera were collected from 8 sites around Mt. Cameroon. From each sites, different sampling points were surveyed given a total of about 12 sampling points in the study. These species were collected from trees and rocks (Table S2). All the collecting points were Georeferenced with a High Sensitive ErexGlobal Positioning System (GPS).

The samples were selected based on the criteria shown on Table 2. The selected species were common to most sites and represent various altitudinal levels on the two flanks of the edifice.

Table 2: Lichen species selected for halogens (fluorine (F), bromine (Br), and chlorine (Cl) analysis.

S/N	Criteria (species abundance at sites, elevation, flanks, morphology)	Species
1.	Foliose Species common to all sampling sites	*Leptogium gelatinosum,*
2.	Species of mid elevation	*Heterodermia obscurata* *Heterodermia jabonica*
3.	Species found on the same sampling (Leeward) site but differ in substrate (tree/rock)	*Parmotrema tinctorum*
4.	Species restricted to the mid and high altitudes	*Flavoparmelia caperata*
5.	Site-specific species (These are species found only in particular sampling points and not seen in any other area)	*Canoparmelia concrescens* *Cladonia sp, Sticta stenroos* *Usnea dasypoga,* *Usnea florida, Usnea articulate*

d) *Sample preparation and analytical procedure*

In the Life Sciences laboratory, University of Buea, the lichen species to be analysed for their halogens (F, Br and Cl) levels, were sorted and curated to remove adhering bark, mosses, other lichen species, soil particles, etc. Following Lorenzini *et al.,* 2006, no washing procedure was done, to avoid the leaching of soluble matter from tissues. The species were put in labeled envelops and oven-dried to constant weight in a Gallenkemp Hot box oven fan size 3 at 60 °C for 48 hours. The different species were put in small zip locked bags and labeled with chemical codes. Samples were chemically analysed by selective ion electrode method, at the department of geology, university of Botswana. A 0.5 g split of each sample was digested with hydrogen fluoride (HF), then aqua regia and the aliquots analysed. The detection limits ranged from 0.01 to 0.02 μg/g. Replicate analyses were performed on selected samples and data quality was excellent with standard deviation values less than 1%. Standards were run between samples and quality control of the analyses was ensured by inserting blanks into the analytical run after 6 samples. Prior to statistical analysis of the geochemical parameters, the data set was regrouped based on the lichen species. The entire data were then log-transformed to normalise skewed distributions. The significance of the difference between means was tested using ANOVA test to compare the concentration of Halogens according to Elevation, Post Hoc Multiple Comparisons Altitudes, Independent Samples t-Test to compare the concentration of Halogens according to substrate types and Box – plot to confirm the test.

III. RESULTS

ANOVA test on the variation in the concentration of halogens across the different elevation revealed that there was a significant difference (p = 0.022) for F and Br and p= 0.030 for Cl at 95% confidence level (Table 2). The box-plots (fig 2) also revealed that Cl concentration are high at lower elevations.

ANOVA test to compare the concentration of Halogens according to Elevation

		Sum of Squares	Df	Mean Square	F	Sig.
Fluorine	Between Groups	17554.069	2	8777.035	4.321	.022
	Within Groups	62966.666	31	2031.183		
	Total	80520.735	33			
Chlorine	Between Groups	7630.711	2	3815.355	3.926	.030
	Within Groups	30129.760	31	971.928		
	Total	37760.471	33			
Bromine	Between Groups	2814.601	2	1407.300	4.322	.022
	Within Groups	10093.429	31	325.594		
	Total	12908.029	33			

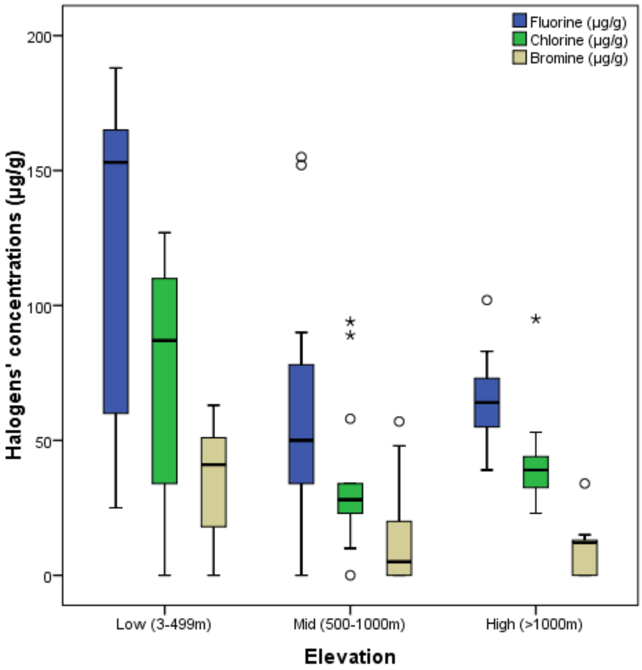

Fig. 3: Box – plot of Halogens concentrations in the different elevations

The Post Hoc Multiple Comparison test (Table 3) shows a significance difference at 0.05 levels of the halogens at low – mid altitude, F (p=0.030), Cl (p=0.027) and no significance difference of Br (p=0.053) at this altitude.

Table 3: Post Hoc Multiple Comparisons

Tukey HSD

Dependent Variable			Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
Fluorine	Low (3-499m)	Mid (500-1000m)	51.849*	19.255	.030	4.46	99.24
		High (>1000m)	51.051*	20.257	.044	1.19	100.91
	Mid (500-1000m)	Low (3-499m)	-51.849*	19.255	.030	-99.24	-4.46
		High (>1000m)	-.799	18.159	.999	-45.49	43.89
	High (>1000m)	Low (3-499m)	-51.051*	20.257	.044	-100.91	-1.19
		Mid (500-1000m)	.799	18.159	.999	-43.89	45.49
Chlorine	Low (3-499m)	Mid (500-1000m)	36.357*	13.320	.027	3.57	69.14
		High (>1000m)	29.364	14.012	.107	-5.12	63.85
	Mid (500-1000m)	Low (3-499m)	-36.357*	13.320	.027	-69.14	-3.57
		High (>1000m)	-6.994	12.561	.844	-37.91	23.92
	High (>1000m)	Low (3-499m)	-29.364	14.012	.107	-63.85	5.12
		Mid (500-1000m)	6.994	12.561	.844	-23.92	37.91
Bromine	Low (3-499m)	Mid (500-1000m)	18.762	7.709	.053	-.21	37.74
		High (>1000m)	22.333*	8.110	.026	2.37	42.29
	Mid (500-1000m)	Low (3-499m)	-18.762	7.709	.053	-37.74	.21
		High (>1000m)	3.571	7.270	.876	-14.32	21.46
	High (>1000m)	Low (3-499m)	-22.333*	8.110	.026	-42.29	-2.37
		Mid (500-1000m)	-3.571	7.270	.876	-21.46	14.32

*. *The mean difference is significant at the 0.05 level.*

Student t-test for the comparism of the halogens with regards to the substrate (Table 4) shows no significance difference in the means of the all the halogens but a slight difference (p= 0.048 at 0.05 levels) in the variance of Cl. The box-plot (fig 3) also confirms the slight difference in Cl.

Table 4: Independent Samples t-Test to compare the concentration of Halogens according to substrate types

		Levene's Test for Equality of Variances		t-test for Equality of Means						
		F	Sig.	T	Df	Sig. (2- tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference	
									Lower	Upper
Fluorine	Equal variances assumed	3.568	.068	-.623	32	.538	-16.533	26.541	-70.595	37.528
	Equal variances not assumed			-.435	3.324	.690	-16.533	38.030	-131.152	98.086
Chlorine	Equal variances assumed	4.234	.048	-1.169	32	.251	-20.933	17.907	-57.408	15.541
	Equal variances not assumed			-.760	3.266	.498	-20.933	27.552	-104.716	62.849
Bromine	Equal variances assumed	2.837	.102	-.761	32	.452	-8.067	10.595	-29.648	13.515
	Equal variances not assumed			-.541	3.340	.623	-8.067	14.914	-52.907	36.774

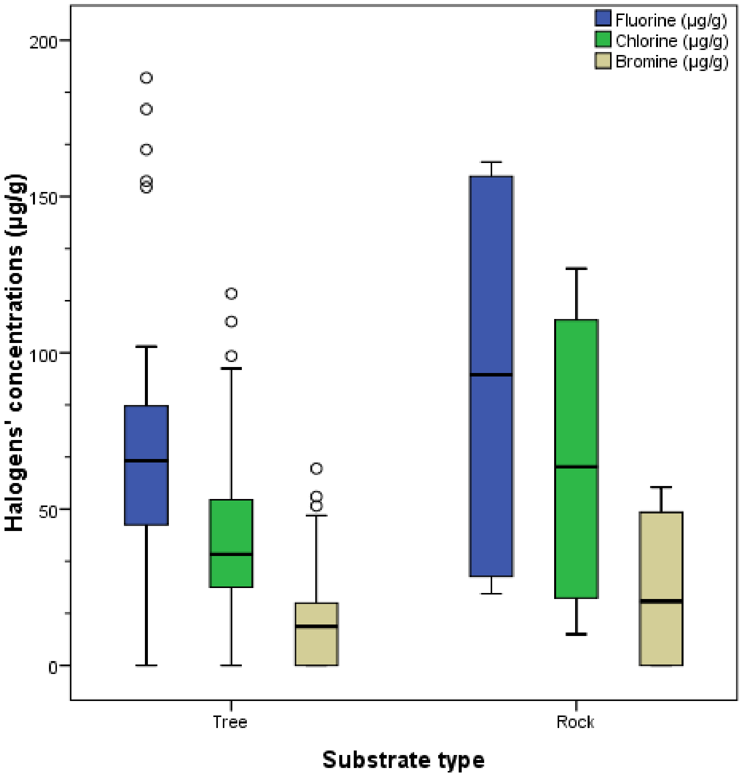

Fig. 3: Box – plot of Halogens concentrations in the substrate types

Table S2 revealed that, of the eight lichen genera used for analyses, *Leptogium* was the most abundant, widely distributed and had very high concentrations of halogens compared to all the other species. *Leptogium gelatinosum* accumulating ability differs between sites. *Leptogium gelatinosum* samples from northern leeward flank (MC 02 from Upper Buea, MC 04 from Bomana and MC 10 and MC 11 from Ekona-Mbenge) show low accumulation of halogens over samples collected from the western windward flank Sasse (MC01 and MC03), Idenau (MC 05 and MC06), Bakingili (MC07) and Batoke (MC08 and MC09).

Although, *Leptogium gelatinosum* recorded highest concentrations, other species like *Heterodermia obscurata, Cladonia sp, Usnea articulate* in BmtUM recorded high concentrations. Lichen species also showed differing accumulating potentials in substrates (*Parmotrema tinctorum* (MC27) a corticolous sample collected in Ekona-Mbenge accumulated more than the saxicolous specimen (MC26) collected in the same point).

All the eight lichen genera showed very high concentrations of F and low levels of Br. F concentration is highest in *Leptogium* (188 μg/g) and lowest in *Parmotrema* (0 μg/gto 23 μg/g). The geochemical analysis of the lichens indicated that F was the most dominant halogen (Fig. S1) with concentrations that range from 25-188 (mean = 78.00 ± 48.68 μg/g). The range for Cl concentration was 10-127 μg/g (mean =47.23 ± 33.37 μg/g), while that for Br, ranges from 0-63 μg/g (mean= 18 ± 19.58).

Fig.S2 shows that, there was highest F- bio-accumulation in *Leptogium gelatinosum* species in Idenau which ranges from (153 to188 μg/g), Batoke (165 μg/g), Bakingili (178 μg/g), Sasse (152 to155 μg/g) and low in Ekona-Mbenge (34 μg/g).

Cl bio-accumulation in the *Leptogium gelatinosum* species in Idenau ranges from (110 to119 μg/g) was highest and lowest in the *Leptogium gelatinosum* of Bomana (23 μg/g), Ekona (33 μg/g) and Hut 1(28 μg/g) (Fig. S3).

Fig. S4, revealed no Br bio-accumulation in the *Leptogium gelatinosum* species in Ekona (0 μg/g) and Bomana (0 μg/g) but higher in Idenau (63 μg/g).

IV. Discussion

Lichens from Mt. Cameroon demonstrated significant compositional variation between species as observed on the multi-element distribution patterns even for those growing in the same area. However, specimens from the same species tend to have similar element concentration patterns. This could be explained by the fact that lichens species selectively accumulated some elements. Similarly, Rani *et al*. (2011) found out that, the estimated nine heavy metals in lichen samples from 12 different sites of Dehradun city by periodic monitoring and spotted Zn, Ni, Cd and Cr were higher in lichens, collected from road side while maximum quantity of Fe, Cu and Al were reported in lichens collected from central sites of the city while the lowest amounts of all the metals were reported in sites farther from city.

The species *Leptogium gelatinosum* with very high concentrations of the halogens in all the sampling sites and even the control area of Mamfe 270 km from Mt. Cameroon has a higher tendency to sequestrate these elements than all the other species recorded in the study. This is in accordance with the study about the suitability of the fruticose lichens *Evernia prunastri, Cetraria islandica* and *Ramalina farinacea* collected from oak trees in a remote area located in the Chianti Region (Tuscany,central Italy), as transplants for biomonitoring trace element, showed that *E. prunastri* has to be preferred for its higher accumulating capacity (Cercasov *et al*., 2002). Different lichens species in different environments have different sequestration potentials, for example, *Ramalina fastigiata* has been used as a bio indicator of the impact of a coal mine in Portugal Jóźwiak, (2012).

The very high concentrations of F in lichens in this study reflects the study of Suh *et al*. (2008) who measured halogen content in melt inclusions at this volcano and their results indicated an average value of 1530 μg/g F and 1270 μg/g Cl. They recorded unusually high F concentrations when compared to glass inclusions from Etna, Hawaii and Piton de la Fournaise. However, the Cl concentrations from Mt. Cameroon were midway between the high values measured for Etna and the low values for Hawaii and Piton de la Fournaise. These exceptionally high values relative to those recorded in this study which maybe an indication that these halogens are an important component of the volatile budget at Mt. Cameroon. These researchers reported that, the concentrations of F in olivine hosted glass inclusion from Mt. Cameroon are the highest known F concentrations for basaltic glass inclusions in the world.

Altitude contributed to the halogens concentration variations as intra-species variations consistently yield high concentrations in samples collected from the downwind SW flank of the volcano. These localities lie in the path of wind bearing volcanic gas plumes from Mt. Cameroon and therefore pin their higher halogen content to passive degassing. Aiuppa *et al.* (2004) reported that, during explosive activity huge quantities of fluorine are deposited with ashes around the volcano up to distances of hundreds of km. Fluorine is present as an adsorbed outer layer on the tephra particles which adsorption occurs by condensation of fluoride onto the tephra particles in the plume above the volcano as it cools. The smaller tephra particles have a larger surface area, so carry more absorbed fluoride than the larger particles". The smaller particles are likely to be carried further from the volcanic source, and so their greater fluorine-carrying capacity extends the zone of potential fluorine poisoning considerably, even to regions where only a 1 mm thick deposit forms. It is advisable to sample and analyse the tephra or vegetation to identify hazardous regions.

This suggests that gases emitted from the volcano are blown south-westwards and are eventually deposited close to the coast resulting in higher halogen content in the lichen species from these areas. More so, the inputs from the sea and from agricultural farms might have increased the high levels in this coastal areas. Studies by *Ndlovu et al*. (2019), on moss and lichen biomonitoring of atmospheric pollution in the Western Cape Province (South Africa) observed halogens to have elevated concentrations for samples collected from areas with close proximity to the ocean. That is, for both moss and lichen samples at areas closer to the ocean had higher halogen concentrations. Their results also confirmed elevated concentration levels for halogens (Cl, I, Br) in areas closest to the ocean. However, since fluorides are released into the atmosphere in large amounts by volcanic eruptions (Bajpai *et al*., 2011) and fluoride (F) compounds, remain in the same chemical form after they are emitted into the atmosphere, the very high levels of F bioaccumulation in this study, might have come from the degassing volcanic winds of Mt. Cameroon. Also, since other sampling points inland shows high concentration of F, degassing winds and ash deposition should have a greater influence.

In this study, even though *Leptogium gelatinosum* was the highest bioaccmulator, *Stictastenroos* and *Heretodemia obscurata* are also good accumulators, while all the *Usnea* species are poor accumulators. According to Brodo *et al*. (2001) fruticose lichens like *Usnea* are very sensitive to air pollutants than foliose lichens and occur only in very pure environments. Out of different growth forms of lichens, foliose lichens are prior to metal accumulation followed by crustose and squamulose lichens (Kar *et al.,* 2014) and least by fruticose lichens (Shukla *et al.,*2014). However, lichens from the *Usnea* species have been used to evaluate heavy metal deposition patterns in the Antarctic (Poblet *et al.,* 2011). Certain epiphytic lichens have been particularly gained attention for their bioaccumulation potential like *Hypogymnia physodes* for bioaccumulation of trace elements and *Pyxine cocoes* for bioaccumulation of metals (Bajpai *et al*., 2012; Daimari *et al*., 2020).

The differing accumulating potentials in substrates of lichen species in this study, (example, *Parmotrema tinctorum* (MC27) a corticolous sample collected in Ekona-Mbenge accumulated more than the saxicolous specimen (MC26) collected in the same point).Contrary, the findings of (Chettri *et al.,*1997), who used the lichen species *Neophuscelia pulla and Xanthoparmelia taractica* to study the bioaccumulation of heavy metals in abandoned copper mines in Greece, where there was a significant correlation between the copper content in the soil(saxicolose) and that of the tree(corticolous) lichen thalli. However, it is for this reason that most studies use epiphytic macro lichens as bio-monitors for air pollutants (Loppi and Pirintsos, 2003). For example, Käffer *et al.* (2011) also reported corticolous lichens as environmental indicators in urban areas in southern Brazil. Furthermore, the no to slight significant difference in means of halogens concentrations with regards to substrates in this study is in accordance with the study of Bajpai *et al.* (2011) in Mandav city in central India illustrated that although most of the metals were absent, or present in insignificant amount in substrates, yet the thallus of lichens had significantly higher concentration of metals such as Cd, Cr, Ni and Zn. Thus it is apparent that the accumulated metals were air borne.

All the eight lichen genera showed very high concentrations of F and low levels of Br. Weinstein *et al*. (1998) reported that, Br and I emissions are not usually of environmental importance and there is virtually no scientific literature on either element. The gas Cl is potentially very hazardous but it is very rare to be released in sufficient quantities to pose a risk (Temple *et al*., 1998). Chlorine concentrations of 0.4 - 2.5 µg/g range cause severe symptoms like upper surface bleaching, epinasty (distorted growth), chlorosis (yellowing) and leaf drop to plants (Temple and Krause, 1998). The Cl/F ratio in the specimens' ranges from 0.29 to 0.94, which is lower than those measured in lichen specimens at Mt. Etna which ranges from 0.51 to 1.46 (Notcutt and Davies, 1989). According to Delmelle *et al.* (1997) changes in the Cl/F ratio may reflect different physico-chemical behaviour of the gases entering the atmosphere. However, Halmer *et al*. (2002) reported that in areas without nearby emission sources, the mean concentrations of fluoride in ambient air are generally less than 0.1*µ*g/g. This was observed from the control area (Mamfe 270 Km) with lower concentrations as compared to those from Mt. Cameroon. Even near emission sources, the levels of airborne fluoride usually do not exceed 2–3 *µ*g/g and in most soils, fluoride is present at concentrations ranging from 20 to 1000 *µ*g/g. This figure can reach several thousand *µ*g/g in mineral soils with natural phosphate or fluoride deposits. Therefore, the atmospheric halogens load at Mt. Cameroon is significantly high and lichens can be potential monitors of this volcanic gas flux.

V. CONCLUSION

Leptogium gelatinosum and *Heretodemia obscurata*are good accumulators, while *Usnea* species poor accumulators and therefore can be used for pollution bio-monitoring programs in Cameroon. The

Leptogium gelatinosum species is therefore a suitable species for monitoring passive degassing at Mt. Cameroon. Also, considering that, lichens of the windward flank of MC accumulated more elemental contents than those from the leeward flanks, shows that wind direction and ash fall contribute largely to pollutant load in lichen species in the windward flanks of mount Cameroon reflecting volcanic degassing as the source. This chemical analysis serves as a baseline data for future studies.

Supplementary Information

The online version of this article offers supplementary material (https://doi.org/xxxxx).

ACKNOWLEDGMENTS

We are grateful for the support by the University of Botswana Gaborone (UBG) where the chemical analyses were performed. We thank Professor Suh Tening Aaron of the University of Buea, who is part of the interdisciplinary research framework under the theme "Understanding the environment of Mount Cameroon". We thank Dr Smith B. Babiaka of the Department of Chemistry, University of Buea, for proof reading of the manuscript.

Conflict of Interests

The authors declare that there is no conflict of interest whatsoever

Funding

This study did not receive any funding.

REFERENCES RÉFÉRENCES REFERENCIAS

1. Ahmad, S., Daud, M., and Qureshi, I. H. (2007). Use of bio-monitors to assess the atmospheric changes. *Proceeding Pakistan Academy of Science* 44 (3): 201-219.
2. Aiuppa A., Bellomo S., D'Alessandro W., Federico C., Ferm M., Valenza M. (2004) Volcanic plume monitoring at Mount Etna by diffusive (passive) sampling. J. Geophys. Res. 109/D21D21 308
3. Ayrault, S., Clochiatti, R., Carrot, F., Daudin, L., and Bennett, J. (2007). Factors to consider for trace element deposition bio-monitoring surveys with lichen transplants. *The Science of the Total Environment* 372: 717-727. https://doi.org/10.1016/j.scitotenv.2006.10.032
4. Bajpai, R., Mishra, G. K., Mohabe, S., Upreti, D. K. and Nayaka, S (2011). Determination of atmospheric heavy metals using two lichen species in Katni and Rewa cities, India. *J. Environ. Biol.* 32, 195–199.
5. Bajpai, R. and Upreti, D (2012). Accumulation and toxic effect of arsenic and other heavy metals in a contaminated area of West Bengal, India, in the lichen *Pyxine cocoes* (Sw.) Nyl. *Ecotox. Environ. Safe.* 83, 63–70, https://doi.org/10.1016/j.ecoenv.2012.06.001.
6. Bargagli, R. (2016). Moss and Lichen Biomonitoring of Atmospheric Mercury: A Review. Science of the Total Environment, 572, 216 31. https://doi.org/10.1016/j.scitotenv.2016.07.202.
7. Bennett, J. P. (2006). Lichens and air pollution. *International Society of Enviromental Botanists* 12 (4).
8. Bjerke, J.W., and Dahl, T. (2002). Distribution patterns of usnic acid-producing lichens along local radiation gradients in West Greenland. *Nova Hedwigia* 75: 487-506. https://doi.org/10.1127/0029-5035/2002/0075-0487
9. Brodeková, L., Gilmer, A., Dowding, P., Fox, H., and Guttová A. (2006). An assessment of epiphytic lichen diversity and environmental quality in Knocksink Wood Nature Reserve. Biology and environment: *Proceedings of the Royal Irish Academy* 106: 215-223. https://doi.org/10.3318/BIOE.2006.106.3.215
10. Brodo, I.M., Sharnoff, S. D., and Sharnoff, S. (2001). Lichens of North America. Yale University Press, New Haven.
11. Cercasov, V., Pantelicˇa, A., Salagean, M., Caniglia, G. and Scarlat, A (2002). 'Comparative study of the suitability of three lichen species to trace-element air monitoring', *Environ. Pollut.* 119, 129–139.
12. Chen, J., Blume, H., and Beyer, L. (2000). Weathering of rocks induced by lichen colonization. *Catena* 39: 121-146. https://doi.org/10.1016/S0341-8162 (99)00085-5
13. Chettri M.K., Sawidis T., Karataglis S. (1997) Lichens as a tool for biogeochemical prospecting. Ecotoxicology and Environmental Safety, 38(3), 322–335.
14. Conti ME, Jasan R, Finoia MG, Iavicoli I, Plá R (2016) Trace elements deposition in the Tierra del Fuego region (south Patagonia) by using lichen transplants after the Puyehue-Cordón Caulle (north Patagonia) volcanic eruption in 2011. Environmental Science Pollution Research International. 23: 6574-6483. Link: https://bit.ly/39K7ajl.
15. Cronin, S.J and Sharp, D.S (2002). Environmental impacts on health from continuous volcanic activity at Yasur (Tanna) and Ambrym, Vanuatu. Int. J. Environ. Health Res. 12,109:123
16. Culberson, C. F., and Culberson, W. L. (2001). Future directions in lichen chemistry. *The Bryologist* 104: 230-234. https://doi.org/10.1639/0007-2745 (2001) 104[0230: fdilc]2.0.CO;2
17. Daimari, R. *et al*. (2020). Biomonitoring by epiphytic lichen species *Pyxine cocoes* (Sw.) Nyl.: Understanding characteristics of trace metal in ambient air of different land uses in mid-Brahmaputra Valley. *Environ. Monit. Assess.* 192, 37, https://doi.org/10.1007/s10661-019-8007-x

18. DeLancey, M. W., and Mark, D. D. (2000). Historical Dictionary of the Republic of Cameroon (3rd ed.). Lanham, Maryland: The Scarecrow Press.
19. Déruelle, B.; N'ni, J and Kombou, R. (1997). Mount Cameroon: an active volcano of the Cameroon Line. *Journal of African Earth Science*, 6 (2): 197-214.
20. Dey S and Giri B (2015). Fluoride fact on human health and health problems: A review. Medical and Clinical Reviews.2:2
21. Diana, P. S. L, Patrícia, V. G and Armindo dos Santos, R (2019). Environmental Health IntechOpen DOI: 10.5772/intechopen.86058
22. Donahue, N.M (2018). Air Pollution and Air Quality. In Green Chemistry: An Inclusive Approach, (Elsevier), pp: 151-176.
23. Garcia MG and Borgnino L (2015). Fluoride in the context of the environment. In: Preedy VR (ed) Fluorine: Chemistry, Analysis, Function and Effects. London: The Royal Society of Chemistry; pp. 3-21
24. Garty, J., Levin T., Cohen, Y., and Lehr, H. (2002). Bio-monitoring air pollution with the desert lichen *Ramalina maciformis*. *Physiologia Plantarum* 115: 267-275. https://doi.org/10.1034/j.1399-3054.2002.1150213.x
25. Godinho, R. M., Wolterbeek, H. T., Verburg, T. G., and Freitas, M. C. (2008). Bio-accumulation behaviour of transplants of the lichen *Flavoparmelia caperata* in relation to total deposition at a polluted location in Portugal. *Environmental Pollution* 151(2): 318-325. https://doi.org/10.1016/j.envpol.2007.06.034
26. Golubev, A., Golubeva, V., Korableva, A., Krylov, N., Kuznetsova, V., Mavrin, S., and Aleinikov, A. (2006). Using of lichens for assessment of uranium atmosphere pollution. *Environment* 3 (36).
27. Grasso, M. F.; Clocchiatti, R.; Carrot, F.; Deschamps, C and Vurro, F. (1999). Lichens as bio-indicators in volcanic areas: Mt. Etna and Vulcano Island (Italy). *Environmental Geology* 37: 207-217.
28. Hauck, M. (2005). Epiphytic lichen diversity on dead and dying conifers under different levels of atmospheric pollution. *Environmental Pollution* 135: 111-119. https://doi.org/10.1016/j.envpol.2004.09.021
29. Hess, D., Coker, D. J., Loutsch, J. M., and Russ, J. (2008). Production of oxalates *in vitro* by microbes isolated from rock surfaces with prehistoric paints in the Lower Pecos Region, Texas. *Geoarchaeology* 23(1): 1–175. https://doi.org/10.1002/gea.20208
30. Jatinder, K.; Roshni, K.; Himanshu, R.; Upreti, D. K.; Tayade, A.; Hota, S.; Chaurasia, O. P., and Srivastava, R. B. (2012). Diversity of lichens along altitudinal and land use gradients in the Trans Himalayan cold desert of Ladakh. *Nature and Science* 10 (4). https://doi.org/10.26438/ijsrbs/v6i1.97104
31. Jitka, S.; Tomás, N.; Jan, R.; Martin, M.; Petra, K.; Ludek, M and Petra S. (2010). The characteristics of rare earth elements in bulk precipitation, through fall, foliage and lichens in the Lesní potok catchment and its vicinity, Czech Republic. *Geochemistry: Exploration, Environment, Analysis* 10: 383-390.
32. Jovans, S. (2008). Lichen bioindication of biodiversity, air quality and climate: baseline results from monitoring in Washington, Oregon and California. General Technical Report.
33. Käffer, M.I., S.M.D.A. Martins, C. Alves, V.C. Pereira, J. Fachel and V.M.F. Vargas, (2011). Corticolous lichens as environmental indicators in urban areas in southern Brazil. Ecological Indicators, 11(5): 1319-1332.
34. Kar, S., Samal, *A.C.,* Maity *J.P.,* Santra, *S.C* (2014). Diversity of epiphytic lichens and their role in sequestration of atmospheric metals. *Int. J. Environ. Sci. Technol.,* 11: 899-908. DOI: 10.1007/s13762-013-0270-8.
35. Jóźwiak, *M* (2012). Macroscopic changes of Hypogymnia physodes *(L.) Nyl.* in antropogenic stress conditions. *Monit. Środ. Przyr.,* 13: 51-62.
36. Larsen, R. S., Bell, J. N. B., James, P. W., Chimonides, P. J., Rumsey, F. J., Tremper, A., and Purvis, O. W. (2007). Lichen and bryophyte distribution on oak in London in relation to air pollution and bark acidity. *Environmental Pollution* 146:332-340. https://doi.org/10.1016/j.envpol.2006.03.033
37. Lawrey, J. D. (1986). Biological role of lichen substances. *The Bryologist* 89:111-122. https://doi.org/10.2307/3242751.
38. Linhares, D., Garcia, P., Ferreira, T., Rodrigues, A (2017). Safety evaluation of fluoride content in tea infusions consumed in the Azores - a volcanic region with water springs naturally enriched in fluoride. Biological Trace Element Research. 179: 158-164.
39. Llop E., Pinho P., Matos P., Pereira M.J., and Branquinho C. (2012). The use of lichen functional group asindicators of air quality in a mediterranean urban environment. *Ecological Indicators* 13: 215-221. https://doi.org/10.1016/j.ecolind.2011.06.005
40. Loppi, S., and Pirintsos, S. A. (2003). Epiphytic lichens as sentinels for heavy metal pollution at forest ecosystems (central Italy). *Environmental Pollution* 121: 327-332. https://doi.org/10.1016/S0269-7491(02)00269-5
41. Lorenzini, G., Grassi, C., Nali, C., Petti, A., Loppi, S., and Tognoti, L. (2006). Leaves of *Pittosporum tobira* as indicators of airborne trace element and PM10 distribution in central Italy. *Atmospheric Environment* 40 (22): 4025-4036.
42. Monge-Nájera, J., María, I. G.,Marta, R. R., and Méndez, V.H. (2002).A new method to assess air

pollution using lichens as bio-indicators. *Revista de Biological Tropical.* 50(1): 321-5.

43. Morris, J., and Purvis, W. (2007). Lichens (Life). London: The Natural History Museum. p.19.
44. Munzi S., Paoli L., Fiorini E., and Loppi S (2012). Physiological response of the epiphytic lichen *Evernia prunastri* (L.) Ach.to ecologically relevant nitrogen concentrations. *Environmental Pollution* 171: 25-29. https://doi.org/10.1016/j.envpol.2012.07.001
45. Ndlovu, N.B., Frontasyeva, M.V., Newman, R.T. and Maleka, P.P (2019). Moss and Lichen Biomonitoring of Atmospheric Pollution in the Western Cape Province (South Africa).American Journal of Analytical Chemistry, 10, 86-102. https://doi.org/10.4236/ajac.2019.103008
46. Nelson PR, Wheeler TB (2016) Persistence of epiphytic lichens along a tephra-depth gradient produced by the 2011 Puyehue-Cordón Caulle eruption in Parque Nacional Puyehue, Chile. Bosque 37: 97-105. Link: https://bit.ly/2X9Mqj0
47. Notcutt, G., and Davies, F. (1989). Accumulation of volcanogenic fluoride by vegetation: Mt. Etna, Sicily. *Journal of Volcanology and Geothermal Research* 329: (333). https://doi.org/10.1016/0377-0273(89)90096-6
48. Pinhoa, P., Bergamini, A., Carvalhod, P., Branquinhoa, C, S., Stofer, S., Scheidegger, C., and Máguas, C. (2012). Lichen functional groups as ecological indicators of the effects of land-use in Mediterranean ecosystems. *Ecological Indicators* 15: 36-42. https://doi.org/10.1016/j.ecolind.2011.09.022
49. Poblet A., Andrade S., Scagliola M., Vodopivez C., Curtosi A., Pucci A.,Marcovecchio J. (1997) The use of epiphytic Antarctic lichens (*Usnea aurantiacoatra* and *U. antarctica*) to determine deposition patterns of heavy metals in the Shetland Islands, Antarctica. Science of the Total Environment, 207(2–3), 187–194.
50. Rani M, Shukla V, Upreti DK, Rajwar GS (2011). Periodic monitoring with lichen Phaeophyscia hispidula (ach.) Moberg in Dehradun city. *The Environmentalist,* 31(4): 376-381.
51. Schwandner, F.M., Seward, T.M., Gize, A.P., Hall, P.A., Dietrich, V.J (2004). Diffuse emission of organic trace gases from the flank and the crater of a quiescent active volcano (Volcano, Aeolian Islands, Italy), *J. Geophys.Res.*, 109, D04301.
52. Shukla, V., Upreti, D. K. and Bajpai, R (2014). *Lichens to Biomonitor the Environment*. 1–185, https://doi.org/10.1007/978-81-322-1503-5.
53. Smodis, B. (2007). Investigation of trace element atmospheric pollution by nuclear analytical techniques at a global scale: Harmonised approaches supported by the IAEA. *Journal of Environmental Management* 85: 121-127. https://doi.org/10.1016/j.jenvman.2006.08.007
54. Srivastava K, Bhattacharya P, Rai H, Nag P, Gupta RK (2015). Epiphytic lichen ramalina as indicator of atmospheric metal deposition, along land use gradients in and around binsar Wildlife Sanctuary, Kumaun, Western Himalaya, *National Conference on Cryptogam research in India: Progress and Prosp.*
55. Stefano, L and Luisa, F (2006). *Lichen Diversity and Lichen Transplants as Monitors of Air Pollution in a Rural Area of Central Italy.* Environmental Monitoring and Assessment: *114:* 361–375. DOI: 10.1007/s10661-006-4937-1
56. Suh, C. E., Luhr, J. F., and Njome, M. S. (2008). Olivine-hosted glass inclusions from Scoriae erupted in 1954–2000 at Mount Cameroon volcano, West Africa. *Journal of Volcanology and Geothermal Research* 169: 1-33. https://doi.org/10.1016/j.jvolgeores.2007.07.004
57. Suh, C. E., Sparks, R. S. J., Fitton, J. G., Ayonghe, S. N., Annen, C., Nana, R., and Luckman, A. (2003). The 1999 and 2000 eruptions of Mount Cameroon: eruption behaviour and petrochemistry of lava. *Bulletin of Volcanology* 65: 267-281. http://dx.doi.org/10.1007/s00445-004-0388-0
58. Temple, P. J., Sun, J. E. J., and Krause, G. H. M. (1998). Peroxyacetyl nitrates (PAN) and other minor pollutants. Recognition of Air Pollutant Injury to Vegetation: A Pictorial Atlas. 2nd Edition. Air and waste management association, Pittsburgh, PA pp 6-1.
59. Van Herk, C. M., Aptroot, A., and van Dobben, H. F. (2002). Long-term monitoring in the Netherlands suggests that lichens respond to global warming. *Lichenologist* 34 (2): 141-154. https://doi.org/10.1006/lich.2002.0378
60. Walker, T. R., Crittenden, P. D., and Young, S. D. (2003). Regional variation in the chemical composition of winter snow pack and terricolous lichens in relation to sources of acid emissions in the Usa river basin, northeast European Russia. *Environmental Pollution*125: 401-412. https://doi.org/10.1016/S0269-7491(03)00080-0.
61. Weinstein, L. H.; Davison, A. W and Arndt, U. (1998). Fluoride. In Recognition of Air Pollutant Injury to Vegetation: A Pictorial Atlas. 2 nd Edition. Pittsburgh, PA; pp 4-1 to 4-27.
62. WHO (2002) Fluorides. Geneva, World Health Organization. Environmental Health Criteria 227, pp. 268.

SUPPLEMENTARY MATERIAL

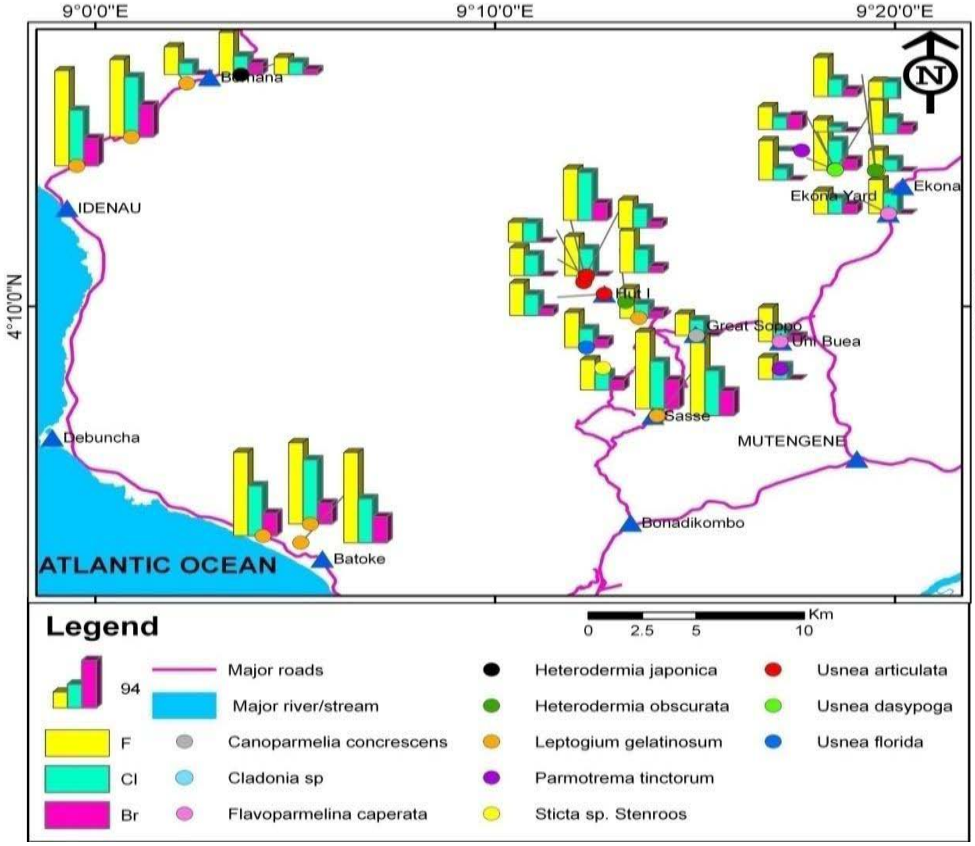

Figure S1: The different Halide concentrations in lichen species studied at the various sampling sites.

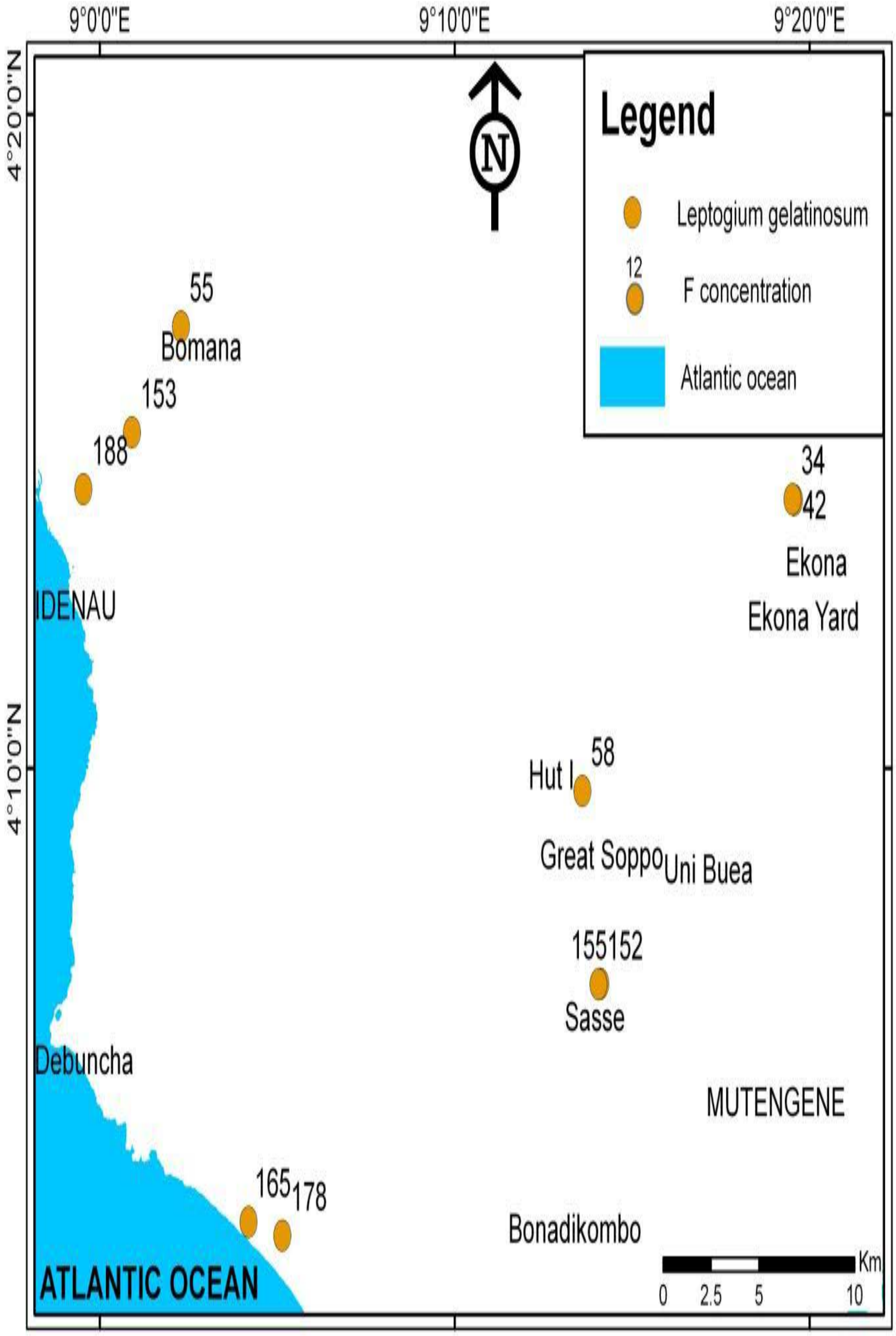

Figure S2: F bio-accumulation in *Leptogium gelatinosum* from different sampling sites on MC.

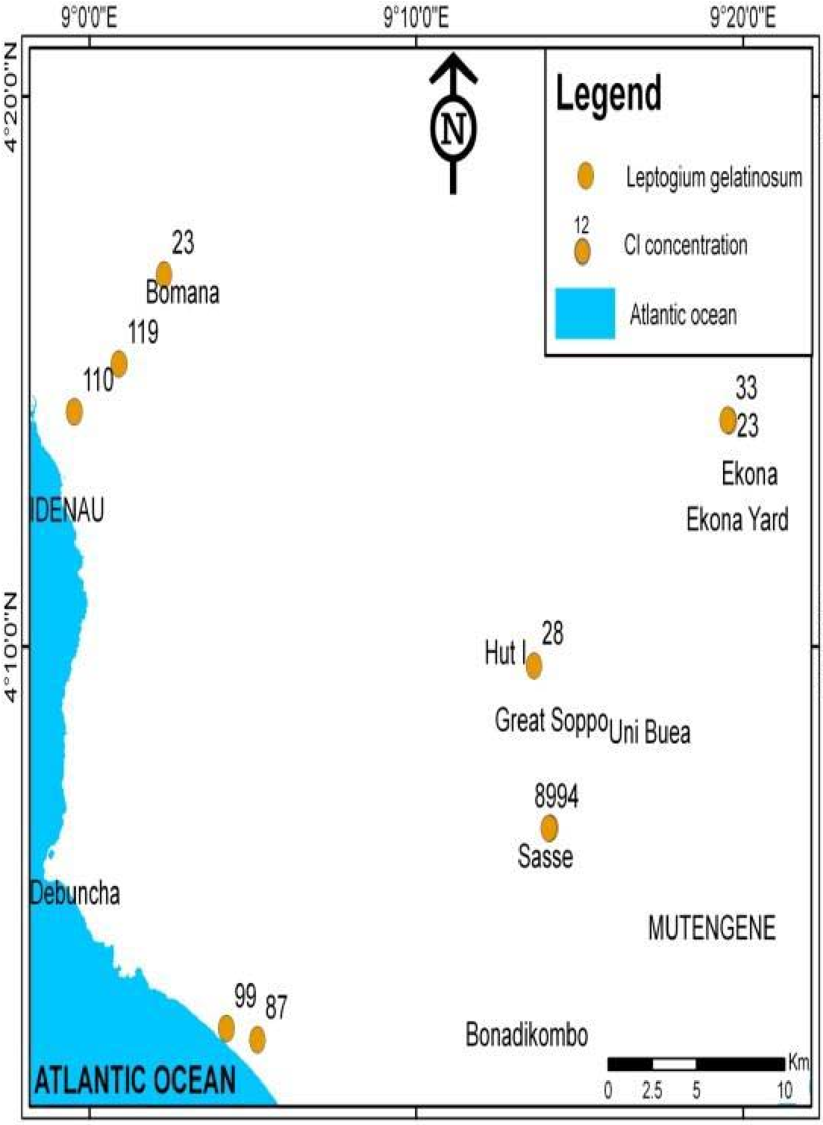

Figure S3: Chlorine bio-accumulation in *Leptogium gelatinosum* species in the different sampling sites on MC.

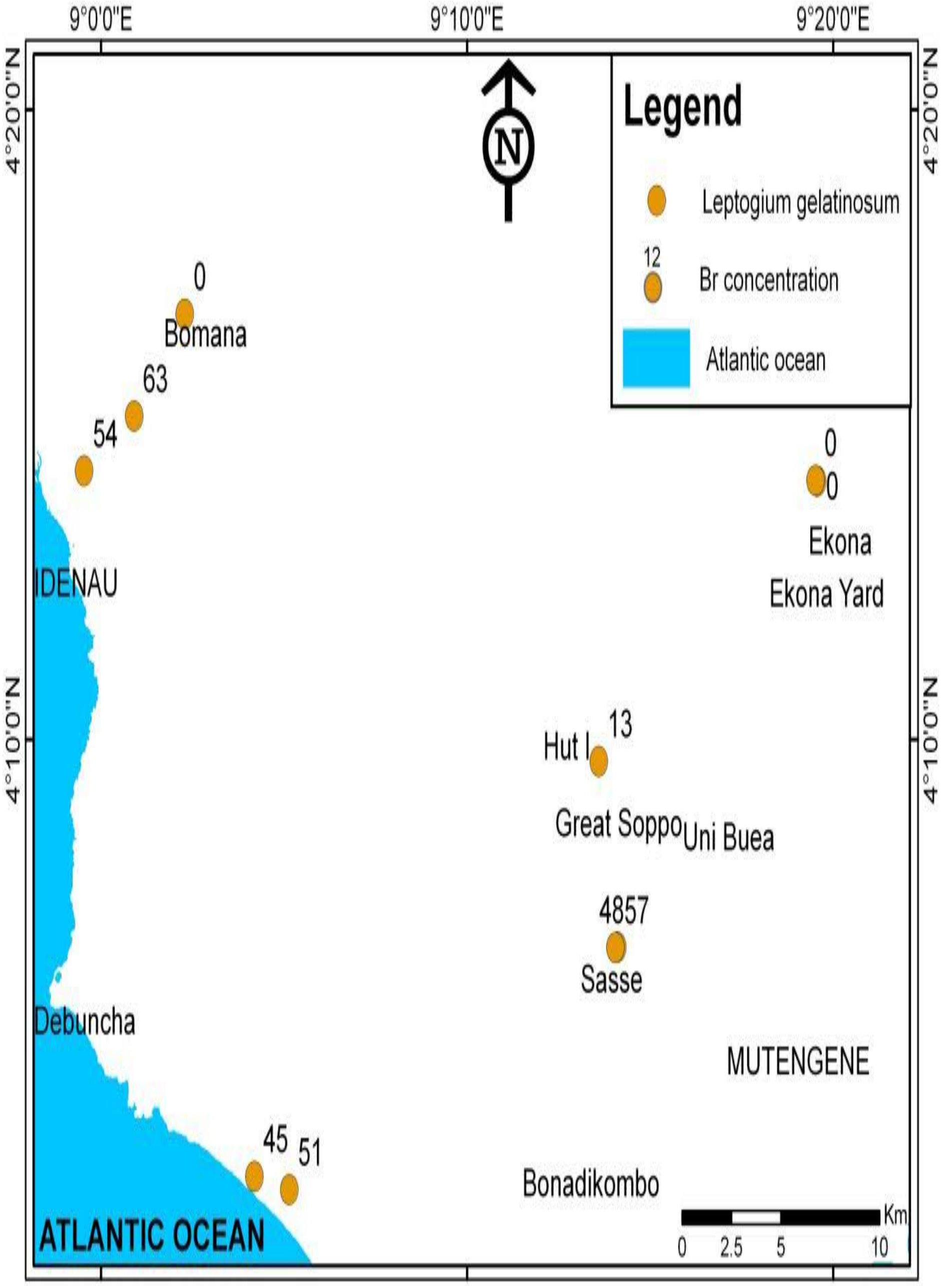

Figure S4: Br bio-accumulation in *Leptogium gelatinosum* at the different sampling sites of MC

LIST OF TABLES

Table S1: Lichen species code, sites and names used for chemical analysis.

Chemical Code	Site	Species name	Chemical Code	Site	Species name
MC 01	BmtSas	*Leptogium gelatinosum*	MC 18	BmtBok	*Sticta stenroos*
MC 02	Bmt UM	*Leptogium gelatinosum*	MC 19	BmtUM	*Cladonia sp*
MC 03	BmtSas	*Leptogium gelatinosum*	MC 20	BmtUM	*Usnea articulata*
MC 04	Boma	*Leptogium gelatinosum*	MC 21	BmtUM	*Usnea articulata*
MC 05	Iden	*Leptogium gelatinosum*	MC 22	BmtUM	*Usnea articulata*
MC 06	Iden	*Leptogium gelatinosum*	MC 23	BmtUM	*Usnea florida*
MC 07	Bakin	*Leptogium gelatinosum*	MC 24	BmtSop	*Canoparmelia concrescens*
MC 08	Batok	*Leptogium gelatinosum*	MC 25	EkLav	*Parmotrema tinctorum*
MC09	Batok	*Leptogium gelatinosum*	MC 26	EkLav	*Parmotrema tinctorum*

MC 10	EkLav	*Leptogium gelatinosum*	MC27	EkLav	*Parmotrema tinctorum*
MC 11	EkLav	*Leptogium gelatinosum*	MC 28	Eklrad	*Parmotrema tinctorum*
MC 12	Mamfe	*Leptogium gelatinosum*	MC 29	EkLav	*Flavoparmelia caperata*
MC 13	BmtUM	*Parmotrema tinctorum*	MC 30	Eklrad	*Flavoparmelia caperata*
MC 14	BmtUB	*Parmotrema tinctorum*	MC 31	EkLav	*Heterodermia obscurata*
MC 15	BmtUM	*Flavoparmelia caperata*	MC 32	EkLav	*Heterodermia obscurata*
MC 16	BmtUB	*Flavoparmelia caperata*	MC 33	EkLav	*Usnea dasypoga*
MC 17	BmtUM	*Heterodermia obscurata*	MC34	Boman	*Heterodermia japonica*

Table S2: Concentration of halogens analyzed for in lichen samples from MC(µg/g).

Chemical Code	Site	Species name	Substrate type	F	Cl	Br
MC 01	BmtSas	*Leptogium gelatinosum*	Tree	155	89	48
MC 02	Bmt UM	*Leptogium gelatinosum*	Tree	58	28	13
MC 03	BmtSas	*Leptogium gelatinosum*	Rock	152	94	57
MC 04	Boma	*Leptogium gelatinosum*	Tree	55	23	0
MC 05	Iden	*Leptogium gelatinosum*	Tree	188	110	54
MC 06	Iden	*Leptogium gelatinosum*	Tree	153	119	63
MC 07	Bakin	*Leptogium gelatinosum*	Tree	165	99	45
MC 08	Batok	*Leptogium gelatinosum*	Tree	178	87	51
MC09	Batok	*Leptogium gelatinosum*	Rock	161	127	41
MC 10	EkLav	*Leptogium gelatinosum*	Tree	42	23	0
MC 11	EkLav	*Leptogium gelatinosum*	Rock	34	33	0
MC 12	Mamfe	*Leptogium gelatinosum*	Tree	25	0	0
MC 13	BmtUM	*Parmotrema tinctorum*	Tree	55	39	12
MC 14	BmtUB	*Parmotrema tinctorum*	Tree	43	27	0
MC 15	BmtUM	*Flavoparmelina caperata*	Tree	55	41	0
MC 16	BmtUM	*Flavoparmelina caperata*	Tree	67	23	11
MC 17	BmtUM	*Heterodermia obscurata*	Tree	83	46	12
MC 18	BmtBok	*Stictastenroos*	Tree	60	34	19
MC 19	BmtUM	*Cladonia sp*	Tree	102	95	34
MC 20	BmtUM	*Usnea articulate*	Tree	64	42	13
MC 21	BmtUM	*Usnea articulate*	Tree	39	38	0
MC 22	BmtUM	*Usnea articulate*	Tree	77	53	0
MC 23	BmtUM	*Usne aflorida*	Tree	69	37	15
MC 24	BmtSop	*Canoparmelia concrescens*	Tree	43	31	0
MC 25	EkLav	*Parmotrema tinctorum*	Tree	0	0	0
MC 26	EkLav	*Parmotrema tinctorum*	Rock	23	10	0
MC27	EkLav	*Parmotrema tinctorum*	Tree	67	32	15
MC 28	Eklrad	*Parmotrema tinctorum*	Tree	45	31	18
MC 29	EkLav	*Flavoparmelina caperata*	Tree	78	23	0
MC 30	Eklrad	*Flavoparmelina caperata*	Tree	67	41	0
MC 31	EkLav	*Heterodermia obscurata*	Tree	90	58	20
MC 32	EkLav	*Heterodermia obscurata*	Tree	77	34	13
MC 33	EkLav	*Usnea dasypoga*	Tree	45	24	27
MC34	Boma	*Heterodermia japonica*	Tree	34	25	10
Mean				78	47	18
Min				0	0	0
Max				188	127	63
SD				49	33	20