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RESEARCH ARTICLE

Implementing the monitoring breakdown structure: native lichens as biomonitors of element deposition in the southern Patagonian forest connected with the Puyehue volcano event in 2011—a 6-year survey (2006–2012)

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Abstract

This study aims to investigate the airborne elements' deposition by using native *Usnea barbata* lichens as biomonitors in the forested areas of Tierra del Fuego (TdF, southern Patagonia), an apparently pristine environment. The present study is linked to the volcanic eruption of the Puyehue-Cordón Caulle which started in north Patagonia in June 2011, which gives rise to long-distance transport of pollutants through the atmosphere at 1700 km from our sampling sites. The monitoring breakdown structure (MBS) was applied to three sampling campaigns in 2006 (baseline) ➔ 2011–2012 (3 and 15 months after the volcanic event, respectively). We have on purpose enhanced the information variety endowment: (i) Seventy-one referenced sites were double sampled; (ii) up to 426 composite lichen samples were collected; (iii) twenty-six elements were measured by neutron activation analysis (As, Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Rb, Sb, Sc, Se, Sm, Ta, Tb, Th, U, Yb, Zn) for samples of 2011 and 2012 campaigns; (iv) thirteen common elements (As, Ba, Ca, Co, Cr, Cs, Fe, K, Na, Sb, Se, U, Zn) were determined in 2006 for the baseline comparison. The natural contamination by tephras is reflected by lichens more clearly in the 2011 campaign, where Ba, Cr, Na, Ca, Cs, and U showed higher median levels compared with the baseline campaign (2006). Ca, K, and Na were the most accumulated elements after the volcano event and could be associated with the volcanic ashes' deposition. Rare earth elements (REEs) showed no significant bioaccumulation levels between 2011 and 2012, indicating their association with higher lithogenic inputs than volcanic ashes. Using the Earth's crust as reference, nine elements (As, Ba, Br, Ca, K, Na, Sb, Se, and Zn) presented moderate/significant mean enrichment factor (EF) values (> 5). The usefulness of *Usnea barbata* as test species for direct biomonitoring oriented kinetic studies in areas characterized by a low human impact is confirmed. Eventually, our results confirm that TdF is not an actual pristine environment as earlier supposed.

Keywords *Usnea barbata* · Native lichens · Monitoring breakdown structure (MBS) · Elements · Atmospheric deposition · Tierra del Fuego · Puyehue-Cordón Caulle volcano · Neutron activation analysis

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Introduction

The traditional air monitoring networks based on particulate matter (PM) samplers generally have very high costs. Therefore, PM dispersion over the territory is classically valued through mathematical models that can have some levels of uncertainty mainly in describing such a complex issue (Perrino et al. 2010; Rai 2016; Kim et al. 2017), and in particular for studies conducted in remote areas of the planet with low contamination levels (Bajpai et al. 2016; Conti et al. 2016). Consequently, there is a growing demand for low-cost air quality monitoring techniques that can be straightforwardly applied aiming to validate dispersion models (Massimi et al. 2019).

The nature of lichens was already the subject of scientific debate as far back as 1876 (Lindsay 1876). The biological monitoring approach has been broadly used for monitoring purposes for many decades (Conti 2008). Among biomonitors, lichens have the aptitude to store contaminants in their tissues and, thus, can be used for the integrated measurement of the concentration of such contaminants in the environment (Garty 1993, 2001; Richardson 1995; Wolterbeek 2002; Conti 2002; Kularatne and de Freitas 2013, Loppi 2014; Lucadamo et al. 2019; Dörter et al. 2020). The main advantage is that lichens can reflect complex synergistic deposition of atmospheric pollutants (i.e., a group of pollutants) providing low-cost spatial and temporal evidence on bioaccumulation patterns at a local or global level (Amman et al. 1987; Getty et al. 1999).

The environment is a complex system (Conti et al. 2018, 2019a), and for the understanding of complexity, it is central to consider the information variety (requisite variety) held by the observer (Ashby 1960). Here we apply the monitoring breakdown structure (MBS) as a model for the management of ecosystems (Conti et al. 2019b). The MBS considers the variety (space) and variability (time) dimensions. It should be noted that several studies on elements' intake in lichens are based on a low quantity of samples and, sometimes, a narrow sampling period.

The present survey relates to the volcanic eruption of the Puyehue-Cordón Caulle (Chile) which started in north Patagonia on June 4, 2011 that gives rise to a long-distance transport by strong winds of tons of ashes, pumice, and sand through the atmosphere at 1700 km from our sampling sites. Volcanic ashes and aerosols are a cause of elemental contamination to the atmosphere ensuing in a long transport of pollutants at both local and global levels (Bagnato et al. 2013; Daga et al. 2014; Conti et al. 2016; Lamela et al. 2019).

For this long-term survey, in 2006, we had selected a presumably uncontaminated remote geographical area aiming to obtain baseline data useful for future management actions that is Tierra del Fuego island (TdF, southern Patagonia, Argentina). Thus, we collected lichens from seventy-one geographically referenced sites in TdF. Subsequently, after the unexpected eruption of the Puyehue-Cordòn Caulle volcano in Chile in June 2011, we sampled the same referenced sites ($n = 71$) in September 2011 and again September 2012 aiming to test the evolution of atmospheric contamination among the sampled years.

The novelty of this study lies in the rationale according to which data have been collected, organized, and then interpreted. See, for instance, Agnan et al. (2017), which, to manage complexity, applied a multivariate approach, coupling frequencies of 92 lichen species and metal bioaccumulation data, performing a scale of resistance/sensitivity to metals for the 43 more common lichen species in French forested areas.

Considering the complex nature of the atmospheric ecosystem, the manuscript outlines a useful framework—the monitoring breakdown structure (MBS)—that both consider the variety (space) and the variability (time) (Conti et al. 2019b, 2020). These dimensions constitute two critical aspects of the ecosystems, and they must be deeply considered in biomonitoring studies. By applying the MBS, then, in this work, we have on purpose enhanced the information variety endowment (twenty-six elements including eight rare earth elements (REEs), up to 426 composite lichen samples, seventy-one sites, about thirteen thousand analytical determinations) in order to have more reliable results about atmospheric elements' deposition and elements' bioaccumulation patterns. The ultimate scope is to give valuable support to the sustainable management of the atmospheric ecosystems meant as a vast, irreplaceable actor in the environmental protection issues (Conti et al. 2019b, 2020). For instance, the estimation of the element deposition could be of significance aiming to avoid likely health effects on humans, mostly for some elements such as As and Cr that are human carcinogens as defined by the International Agency for Research on Cancer (IARC 1990, 2012).

The selected species for the passive biomonitoring method is the *Usnea barbata* (L.) Weber ex F.H. Wigg lichen (typically called *old man's beard*), which abundantly grows in the central south areas of TdF. *Usnea barbata* already demonstrated excellent suitability for biomonitoring purposes in urban, uncontaminated sites and volcanic areas (Grasso et al. 1999; Culicov and Yurukova 2006; Conti et al. 2009, 2012; Agnan et al. 2014; Gandois et al. 2014).

In this survey, we have evaluated the influence of the volcanic eruption on the regional atmospheric deposition determining the atmospheric deposition of 26 elements (As, Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Rb, Sb, Sc, Se, Sm, Ta, Tb, Th, U, Yb, Zn) by neutron activation analysis (NAA) 3 months (2011) and 15 months after the volcano event in June 2011. We compared our results with baseline data (first sampling campaign, 2006) in which we determined thirteen common elements (As, Ba, Ca, Co, Cr, Cs, Fe, K, Na, Sb, Se, U, Zn) in native *U. barbata* lichens. The patterns of bioaccumulation among the three sampling campaigns before and after the volcanic eruption, including REEs and enrichment factors, are thoroughly discussed.

Materials and methods

Rationale: the monitoring breakdown structure

As already described, the atmosphere is a complex system, i.e., approximately, a system "made up of a large number of parts that interact in a nonlinear relationship" (Simon 1962).

Starting from the seminal works of Simon, a focus on the complex nature of the atmospheric ecosystem is necessary for the Anthropocene era in which appears a dramatic call to connecting efficiency and efficacy to viable sustainability (Simone and Barile 2015, 2016). Thus, maintaining air quality/safe sustainability standards in the Anthropocene era claims for more stringent rules for preserving the environment and people's health. To this aim, it is of fundamental significance to investigate and manage the atmospheric ecosystem coherently with its intrinsically complex nature stressed by variety and variability. Thus, in this study, we collect and organize data according to the variety and variability dimensions emphasizing the ecosystem complexity. The variety is a synchronous dimension, i.e., it is related to space, and it requires different sampling sites at the same time. In this study, variety signifies that in many places at the same time, different levels of elements can be accumulated in lichens and then detected. Instead, variability is a diachronic dimension, and it is linked to the possibility of a phenomenon which shows variants over time. In this study, variability refers to a change in element bioaccumulation levels in lichens over time in the same area (2006 ➔ 2011–2012). "The number of variations that the system presents at a given time and the degree of change over time is a measure of complexity" (Conti et al. 2019b).

Considering variety and variability drives to the proposed complexity-based conceptual framework: the monitoring breakdown structure (MBS). This approach is distinct from several studies on the element's bioaccumulation in lichens that were conducted in a narrow sampling period and, sometimes, with reduced numerosity of samples. The MBS conceptual model keeps into account the variety (space) and variability (time) dimensions of the ecosystem under study (TdF, southern Patagonia). It concerns (i) the space breakdown structure with its three levels of variety: 1st = 71 sites, 2nd = the selected biomonitor *U. barbata*, and 3rd = 26 elements. (ii) The time-space monitoring matrix (Fig. 1) involves the variety dimension: i.e., the forested areas; and the variability dimension: time, e.g., three sampling campaigns, 2006, 2011, and 2012 (Conti et al. 2019b, 2020).

Building the sample consistently with the complex nature of the atmospheric ecosystem is crucial to have a satisficing (if not optimal) understanding of the ecosystem under study. According to Ashby's Law (1960), the knowledge of a complex system (requisite variety) depends on the information variety endowment owned by the observer/decision-maker.

In summary, to understand and effectively manage a complex system, the higher the complexity of the system increases (i.e., its variety and variability), the higher the level of the information variety (i.e., abundance and diversity of the information endowment) owned by the observer/decision-maker must increase. Due to its compatibility with the atmospheric ecosystem complexity, in terms of variety and variability dimensions, the MBS improves the observer's information variety endowment about the positive/negative features of the lichens as biomonitors of atmospheric pollution. The MBS, being well articulated along the two essential dimensions of space and time, contributes to decreasing the gap between the requisite variety and the information variety endowment of the observer and leads to more favorable results in managing the atmospheric ecosystem in a supposedly uncontaminated geographical area.

Study area

Tierra del Fuego island is an important ecosystem that covers a vast area where large stands of old-growth forests, alpine meadows, water systems, fjords, and snow-capped mountains are present, as well as an ample range of wildlife and biodiversity (Conti et al. 2009). The capital of TdF, with about 60,000 inhabitants, is Ushuaia (54° 48′ 23″ south latitude and 68° 18′ 17″ west longitude), the southernmost city in the world, and the greatest city of TdF island. The other large city is Río Grande, over the Atlantic coast, and Tolhuin is a small village between Ushuaia and Río Grande (see Fig. 2).

The northeast is characterized by powerful winds and scarce precipitation (cool semidesert); in the south and west, it is very breezy, foggy, and humid for most of the year. TdF region is listed as a subpolar oceanic climate with tiny, cool summers and long and cloudy winters.

The total forested area is 630.000 hectares (ha), of which 430.000 ha is of *Nothofagus pumilio* (usually named Lenga), and 200.000 ha is of *Nothofagus antarctica* (often called Ñire). *Nothofagus pumilio* is the most common timber native species from southern Patagonia (Martinez Pastur et al. 2000). It has been reported that forest environments can affect elements' bioaccumulation patterns in lichens (Gandois et al. 2014). *Usnea barbata* grows well on these species. In the last decades, the government of Argentina promoted the installation of a few manufacturing and assembling industries, notably the electronic ones in Rio Grande. Crude oil exploitation activities also interest Rio Grande port while Ushuaia is the principal port for Antarctic tourism and maritime traffic. Lichens, as well known, can act as a biomonitor for vehicular emission of metals in contaminated areas (Huang et al. 2019; Liu et al. 2017; Boonpeng et al. 2020). However, the vehicle traffic in TdF is meager, i.e., a maximum of 30 cars per hour between Ushuaia and Rio Grande (Pino et al. 2010).

Sampling sites and sampling procedure

Seventy-one lichen composite double samples of *U. barbata* were collected from the trunk of trees (*N. pumilio and N. antarctica*) with inclination < 10% at the height of more than 1 m above ground level. The collection sites were established

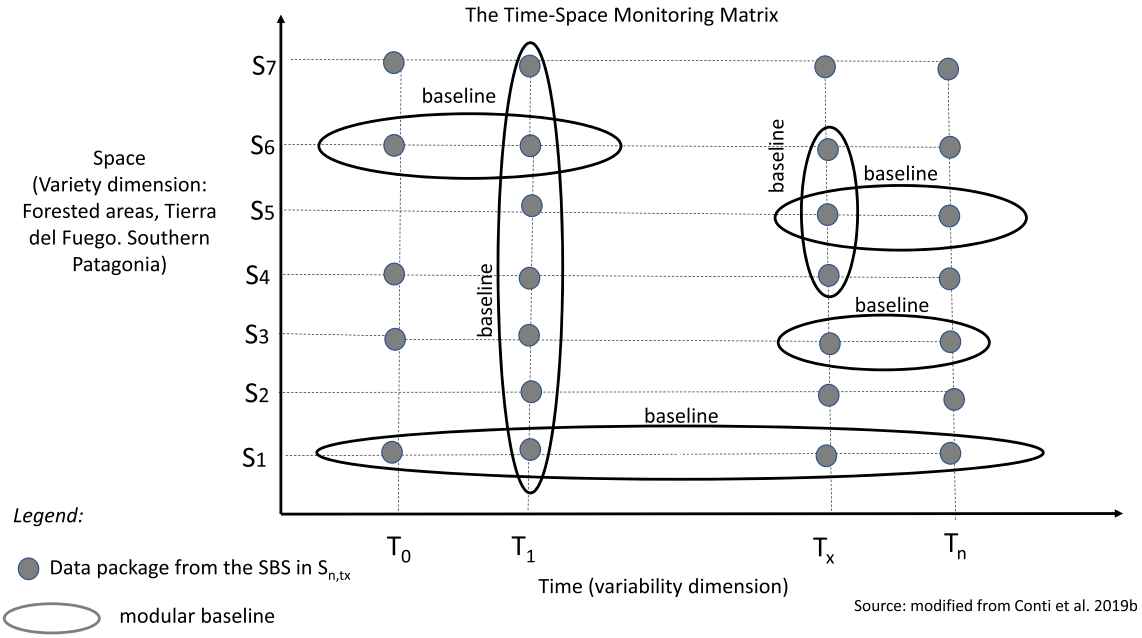

Fig. 1 The monitoring breakdown structure conceptual model: the TimeSpace Monitoring Matrix (modified from Conti et al. 2019b)

at least 150 m away from the roads. *Usnea barbata* lichens were sampled at about 10 km among sites (see Table 1 and Fig. 1 for sites' description). Samples arise from individual *thalli* ($n = 10$) randomly collected from five to ten different trees within 100 m from the geographically referenced point (for sampling details, see Bargagli and Nimis 2002; Conti et al. 2009; for sampling requirements, see also Adams and Gottardo 2012; and Wiersma et al. 2019). Sampling procedures started after at least 5 days after raining, and care was exerted to choose *thalli* at a similar stage of development. Lichens were sampled in three monitoring campaigns carried out in September 2006 and again, after the volcano eruption in June 2011, in September 2011 and 2012 in the same geographical referenced sites (Table 1).

In the laboratory, samples were sorted to remove extraneous material (i.e., soil particles, mosses, and other lichen species) with nylon tweezers under a binocular microscope (Conti et al. 2004). Different sampling strategies may provoke essential changes in element contents; thus, lichens were not washed. As previously reported, lichen washing can alter the

Fig. 2 Sites' map

Table 1 Forested areas and sampling sites for the three monitoring campaigns in Tierra del Fuego (southern Patagonia)

Forested areas	Sampled sites (n.)	Range Lat S	Range Long W	Distance[a] (km)	Map area[b]
Radman - Rio Grande	4	54° 00′ 01″ 53° 57′ 04″	068° 35′ 42″ 068° 13′ 33″	33	A
Rio Grande -Yeguin	11	53° 57′ 29″ 54° 21′ 31″	067° 41′ 37″ 067° 15′ 09″	109.8	B
Rio Grande -Tolhuin	8	53° 56′ 36″ 54° 29′ 15″	067° 31′ 53″ 067° 10′ 58″	92.8	C
Ruta 3 - Irigoyen river	7	54° 16′ 40″ 54° 29′ 12″	067° 06′ 10″ 066° 26′ 56″	80	D
Ushuaia - Ruta 3	7	54° 45′ 45″ 54° 37′ 04″	068° 11′ 40″ 067° 25′ 11″	70	E
Tolhuin	7	54° 33′ 13″ 54° 30′ 42″	067° 13′ 03″ 067° 11′ 42″	18.6	F
Punta Moat	10	54° 58′ 32″ 54° 52′ 50″	066° 44′ 39″ 067° 43′ 40″	76.7	G
Proximity to Ushuaia	7	54° 49′ 44″ 54° 49′ 05″	068° 21′ 39″ 068° 11′ 13″	22	H
National Park of Tierra del Fuego	5	54° 51′ 20″ 54° 50′ 02″	068° 34′ 35″ 068° 25′ 24″	25.3	I
Rancho Hambre	5	54° 51′ 12″ 54° 44′ 45″	067° 30′ 03″ 067° 48′ 11″	28	L

[a] Linear distance between the first and the last sampling site of the studied area

[b] Marks in the map reported in Fig. 2

elements' lichen composition (Conti and Cecchetti 2001), provoking the elimination of particulate matter (PM) and, in this case, the removal of the fine pyroclastic material incorporated by lichens. The dry weight calculation (30 replicates) was conducted by oven drying 1 g of fresh material at 60 ± 2 °C until constant weight. Mineralization procedures, element determinations by sector field inductively coupled plasma mass spectrometry (SF-ICP-MS), figures of merit, and CRM validation for 2006 samples, have been previously reported (Pino et al. 2007; Bocca et al. 2007; Conti et al. 2009).

Neutron activation analysis

After manually cleaning lichen samples of foreign materials, the samples were ground with an automatic Spex CertiPrep cryogenic mill and then freeze-dried. Approximately 300 mg of material was pelletized and wrapped in aluminum foil for irradiation together with certified reference materials, NIST 1633b Coal Fly Ash, IAEA V-10 Hay Powder, and IAEA Lichen 336.

The irradiations were performed at the RA-3 reactor (thermal flux 3.10^{13} cm^{-2} s^{-1}, 8 Mw) of the Ezeiza Atomic Centre (Argentine National Atomic Energy Commission) for 5 h. Twenty-six elements As, Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Rb, Sb, Sc, Se, Sm, Ta, Tb, Th, U, Yb, and Zn were determined using instrumental NAA.

Two measurements, after 7 and 30-day decay, were done using GeHP detectors (30% efficiency, 1.8 keV resolution for the 1332.5 keV ^{60}Co peak). From each sample gamma spectra, elemental concentrations were calculated using a software developed at the NAA laboratory.

For quality control purposes, GBW07405 soil and WEPAL 2011.4 sample 4 Grass were used as control samples (Bode and Van Dijk 1997). The NAA results were within the uncertainty margins informed for the reference materials, thus showing good accuracy (see Supplementary Material Table S1).

Enrichment factor and contamination factor

The enrichment factor (EF) of an element provides information regarding its origin, so it is often used as a first exploratory step in the interpretation of the analytical data. It is defined as the double ratio of the element of interest in the sample to a reference element in the sample divided by the ratio of the same elements in a reference material (e.g., earth crust, soil, seawater):

$$\mathrm{EF} = \frac{\left(\frac{X}{C}\right)\text{sample}}{\left(\frac{X}{C}\right)\text{reference material}}$$

where X is the element of interest, and C is the reference element. For atmospheric aerosols, earth crust or soil is taken as reference material and Al, Fe, Sc, Ti, or Zr as geochemical tracers of soil erosion, considered the main source of

particulate matter.

In this work, for EF calculation, we have used Fe as a reference element, and Mason's (1966) elemental crustal concentrations as reference. For elements of probable marine origin (e.g., Br), the reference element is usually Na, and the reference material is seawater. Adopting a conservative approach, an EF of ten or higher is indicative of an anthropogenic source while a value close to one points out natural (crustal, soil, seawater) origin. The contamination factor (CF) was calculated according to Conti and Cecchetti (2001).

Statistical analysis

Two composite native lichen samples for each site were analyzed separately (double sampling, i.e., 71 × 2 samples) in the three sampling campaigns (2006, 2011 and 2012).

Kruskal–Wallis (KW) test was first applied for testing significant differences among the three sampling periods. If significant differences were detected, multiple comparison median tests (MCMT) were then applied for the comparison among the three sampling campaigns. Results of MCMT are reported with letters a, b, and c when appropriate in the box and whisker plots reported in Figs. 3, 4, and 5 (Conover 1999). The aim was to determine the elements' bioaccumulation trend starting from the baseline elements determined in the biomonitor before the volcanic eruption in 2006 to the element's accumulation measured after the eruption (2011 ➔ 2012). For the comparison of elements' bioaccumulation patterns measured in 2011 vs. 2012, after the volcanic eruption, we used the Mann–Whitney (MW) test. Data analysis was made by using the software R 3.6.2. (R Core Team 2019) and the Agricolae Package (de Mendiburu 2019).

Results and discussion

Results confirmed data homogeneity for duplicate samples. Thus, we merged data of duplicated samples. The descriptive statistics of the element concentrations in native lichens collected after 3 months (2011) and 15 months (2012) of the volcano eruption are reported in Tables 2 and 3, respectively. Table 4 reports baseline data measured in native lichens collected in 2006 before the volcanic eruption in the same referenced sites.

Impact of the volcanic eruption on the regional atmospheric deposition

Firstly, we assessed the effect of the eruption on the TdF atmospheric deposition. Thus, we compared our results with baseline levels we detected for the common elements in native lichens in the same sites in 2006. Figures 3, 4, and 5 show the box and the whisker plots of the element concentrations in native lichens in the central south forested areas of TdF (southern Patagonia) for the three sampling campaigns, i.e., 2006, 2011, and 2012. In this study, for comparison purposes, we used the elements' median concentration values in order to achieve a more conservative approach.

Usnea barbata is an excellent bioaccumulator of elements, as reported in several studies (Conti et al. 2012). For As (Fig. 3), the median levels we determined resulted not significantly different among the three sampling campaigns (2006 ➔ 2011–2012) (KW = 4.29, n.s.). The median concentrations of As in the three sampling campaigns were 0.50, 0.55, and 0.46 μg g^{-1}, respectively (Tables 2, 3, and 4) showing a constant trend of bioaccumulation in lichens in 6 years of the survey. Thus, excluding other possible sources of emissions, it appears that the volcanic eruption has not affected the As levels in the sampled lichens. Comparing the obtained As levels with those previously reported for the transplanted lichens in the north area of TdF (Conti et al. 2016), our median values match those determined in 2006 and 2012 for transplants showing a similar bioaccumulation trend. Recently, it has been reported that geothermal processes on volcanos can influence the As concentration in water ecosystems (Lamela et al. 2019).

Ba (Fig. 3, Tables 2, 3, and 4) showed higher median levels in 2011 (27.10 μg g^{-1}, see box and whisker plot marked "a" in Fig. 3) with respect to the 2012 sampling campaign (22.0 μg g^{-1}, letter b in Fig. 3) and lower levels before the volcano eruption in 2006 (15.38 μg g^{-1}, letter c in Fig. 3) (KW = 24.86, $p < 0.001$).

Ca (Fig. 3, Tables 2, 3, and 4) showed lower median baseline levels in 2006 (2156 μg g^{-1}, see box and whisker plots marked with letter "b" in Fig. 3) with respect to those determined after the eruption in 2011 (4369 μg g^{-1}) and 2012 (4000 μg g^{-1}) (KW = 21.47, $p < 0.001$). The Ca median levels were higher after the eruption in 2011 and 2012, showing a similar constant trend (see letters "a" in Fig. 3). In general, the transplanted lichens in the north area of Tierra del Fuego (Conti et al. 2016) showed lower Ca median bioaccumulation levels (i.e., 1786, 2078, and 1582 μg g^{-1} in 2006, 2011, and 2012 respectively) than those determined in this study.

Co (Fig. 3, Tables 2, 3, and 4) showed no significant differences (KW = 2.84 n.s.) among the three sampling campaigns being its atmospheric deposition quite constant before and after the eruption in 6 years of this survey, i.e., 0.30, 0.34, and 0.26 μg g^{-1} in the 2006, 2011, and 2012 sampling campaigns respectively. These values are lower than those obtained with transplants in the non-forested northern areas after the eruption (i.e., 0.467 μg g^{-1} in 2011 and 0.428 μg g^{-1} in 2012 respectively). Cobalt uptake is usually regulated by lithogenic inputs and mostly derived from atmospheric deposition (Manta et al. 2002); it is an essential trace element for plants with a function associated with defense mechanisms of frost and aridity resistance (Freitas and Pacheco 2004).

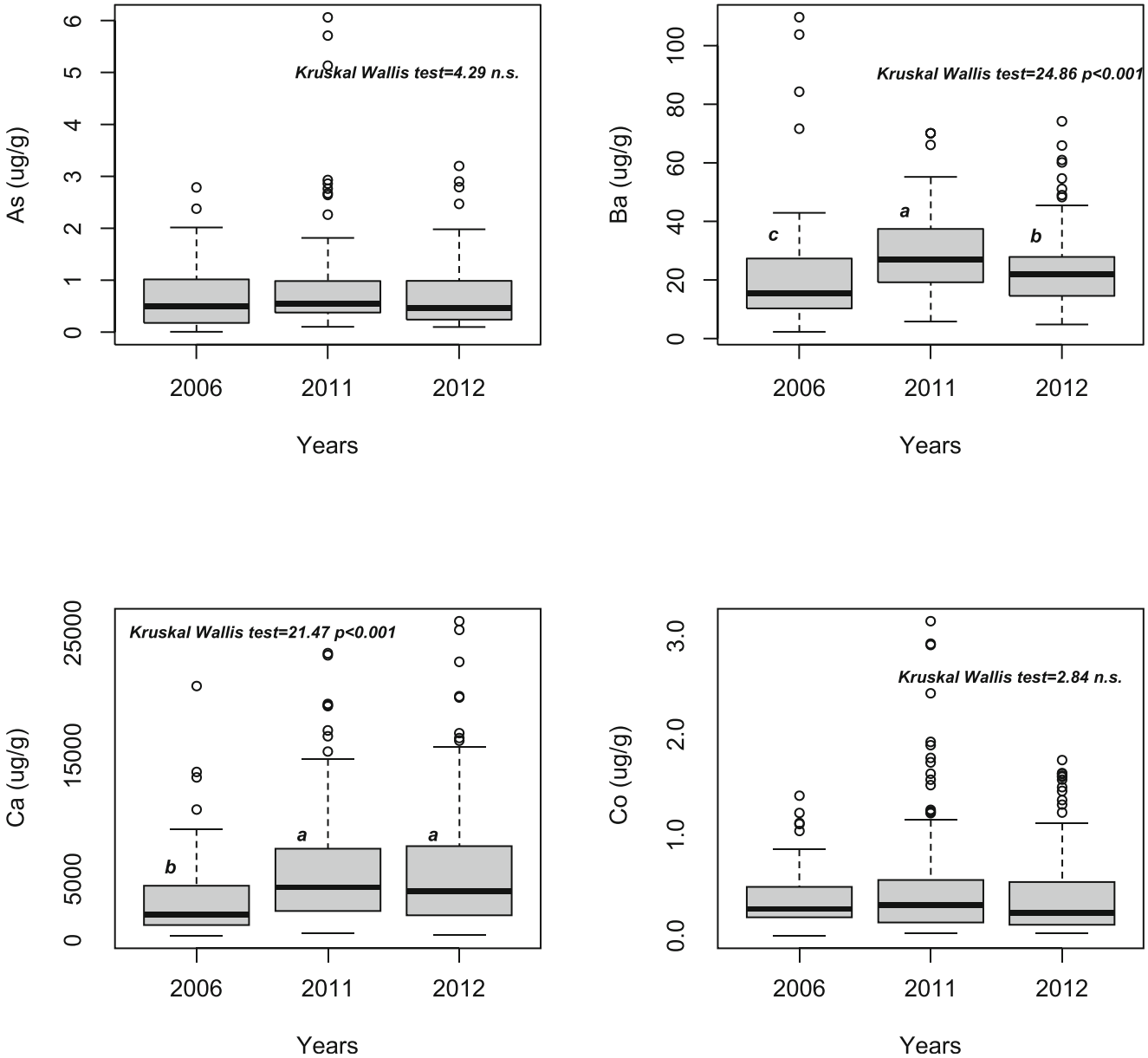

Fig. 3 Box and whisker plots of As, Ba, Ca, and Co concentrations in native lichens in the central south forested areas of Tierra del Fuego for the three sampling campaigns (2006 ➔ 2011–2012). The black line is the median level, and the boxes represent the first and the third quartile, while the whiskers are set to ± 1.5 times the interquartile interval. These levels should match the minimum and maximum levels in the absence of outliers and/or extreme levels

Cr (Fig. 4, Tables 2, 3, and 4) showed the higher median levels after the eruption in 2011 (4.95 μg g^{-1}, letter a in Fig. 4) followed by lower levels in 2012 (2.28 μg g^{-1}, letter b in Fig. 4) and the lowest values before the eruption in 2006 (0.67 μg g^{-1}, letter c) (KW = 143.6, $p < 0.001$).

Thus, we detected Cr levels in native lichens from the central forested areas higher by a factor of 7.39 after 3 months (2011), and a concentration factor (CF) of 3.40 after 15 months (2012) of the volcano eruption, compared with the baseline levels determined before the volcanic event (September 2006). This trend is like those we obtained in the northern areas of TdF in transplanted lichens, where the CFs were very high, i.e., 14.8 (2011) and 8.25 (2012) with respect to baseline levels (2006) (Conti et al. 2016).

Ce (Fig. 4, Tables 2, 3, and 4) showed similar higher median levels after eruption in 2011 (0.095 μg g^{-1}) and 2012 (0.084 μg g^{-1}) (see letter a for both years in Fig. 4) compared with 2006 levels (0.06 μg g^{-1}, letter b) (KW = 17.18, $p < 0.001$). A similar trend was observed for the non-forested areas in the north of TdF, where the median levels in transplanted *U. barbata* samples resulted slightly higher after the volcano eruption than a baseline site (2006) (Conti et al. 2016).

Fe (Fig. 4, Tables 2, 3, and 4) showed no significant median differences among the three sampling campaigns (KW =

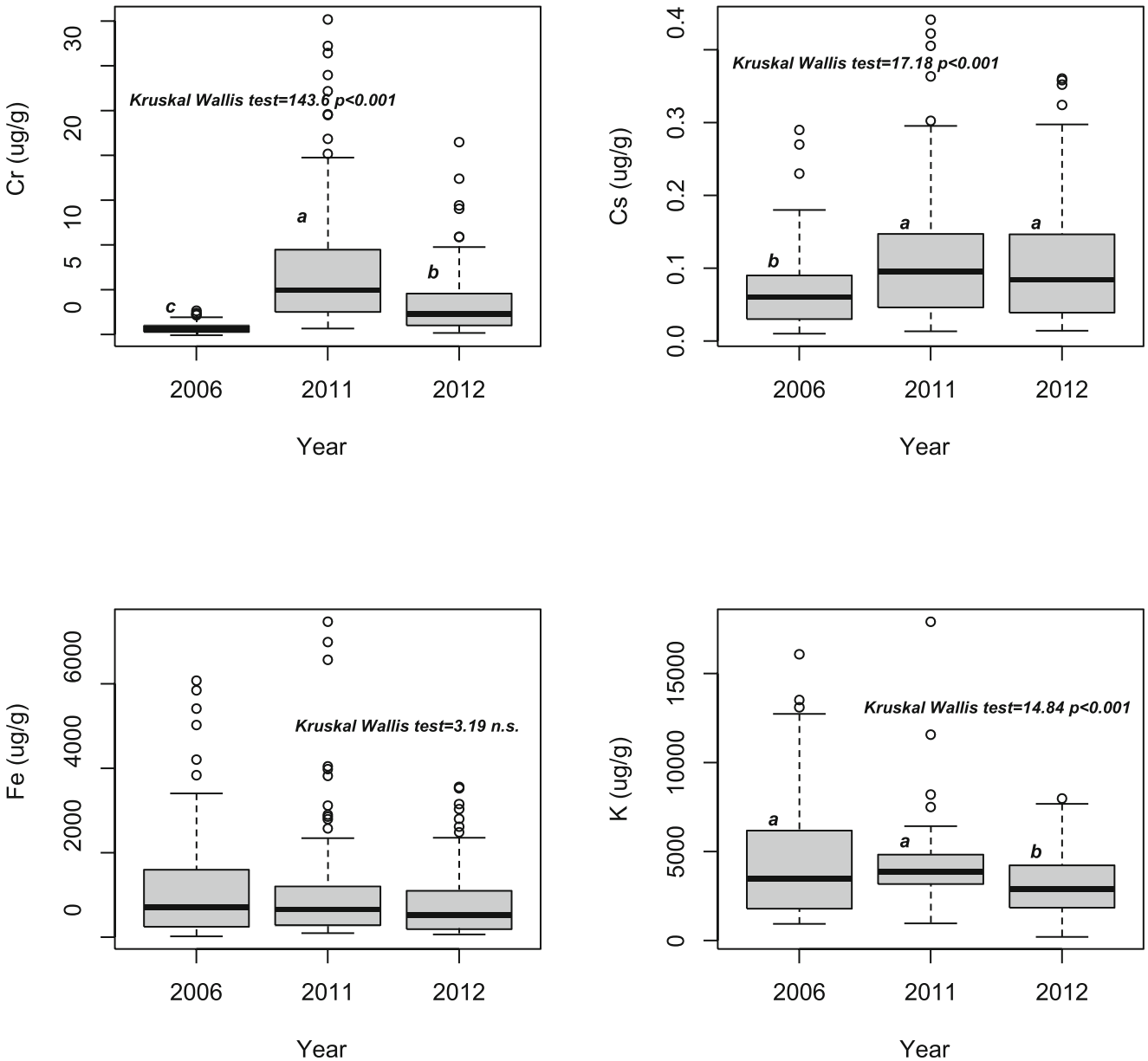

Fig. 4 Box and whisker plots of Cr, Cs, Fe, and K concentrations in native lichens in the central south forested areas of Tierra del Fuego for the three sampling campaigns (2006 ➔ 2011–2012). See Fig. 3 legend for plot's graphic representation

3.19 n.s.) (i.e., 714, 639, and 516 μg g^{-1} for 2006, 2011, and 2012, respectively). A similar trend was also observed for the north sampled areas for transplanted lichens, where differences among the sampling collection were not significant (Conti et al. 2016). Fe is regularly correlated with coarse atmospheric particles and particularly with their input due to the soil particle deposition. Moreover, typical lithogenic elements (Fe and Mn) from eolian dust samples and topsoils could act as indicators of a natural weathered material source (Gaiero et al. 2003).

K (Fig. 4, Tables 2, 3, and 4), conversely, showed similar concentrations in lichen samples in 2006 and 2011 sampling periods (i.e., 3473 and 3844 μg g^{-1}, respectively. See letter a, Fig. 4), while resulted in being lower after 15 months of exposure in lichens (2900 μg g^{-1} in 2012, letter b, Fig. 4) (KW = 14.84, $p < 0.001$).

Significant accumulation differences (KW = 57.4, $p < 0.001$) were observed for Na among the sampling campaigns (see letters a, b, and c, Fig. 5). The highest median levels were observed after the eruption in 2011 (i.e., 1367 μg g^{-1}) followed by the levels obtained in 2012 (i.e., 1084 μg g^{-1}), while the lowest levels were detected in 2006 (768 μg g^{-1}). These results evidence a trend of Na increment after the volcano eruption in the native lichens evidencing the connection with the event. A similar trend for Na was also observed for transplanted lichens in the north desertic area of

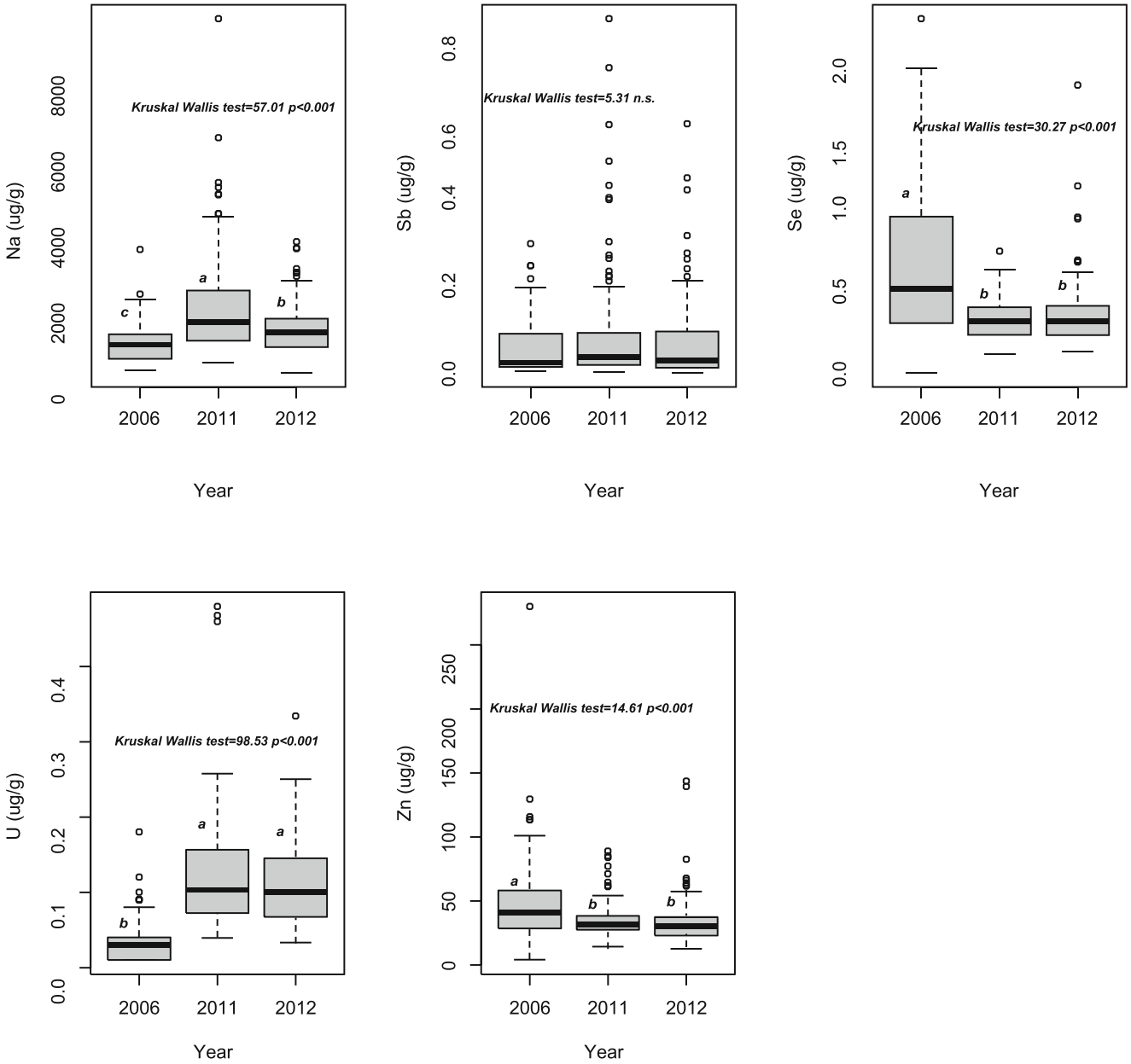

Fig. 5 Box and whisker plots of Na, Sb, Se, U, and Zn concentrations in native lichens in the central south forested areas of Tierra del Fuego for the three sampling campaigns (2006 ➔ 2011–2012). See Fig. 3 legend for plot's graphic representation

TdF island. Na showed higher levels in 2011 (1839 μg g^{-1}) and 2012 (1410 μg g^{-1}) in transplants, compared with 2006 baseline data (897 μg g^{-1}) (Conti et al. 2016).

Sb (Fig. 5, Tables 2, 3, and 4) showed non-significant differences among the three sampling campaigns being the concentrations quite constant in 6 years of the survey (0.03, 0.042, and 0.033 μg g^{-1} in 2006, 2011, and 2012 sampling campaigns respectively).

Se (Fig. 5, Tables 2, 3, and 4) showed higher median levels ($KW = 30.27$ $p < 0.001$) in native lichens in 2006 (0.53 μg g^{-1}, see letter a in Fig. 5) than levels determined after the eruption, which resulted in being similar (i.e., 0.331 and 0.333 μg g^{-1} in 2011 and 2012 respectively, see b in Fig. 5). Se has one of the narrowest ranges between dietary deficiency (< 40 μg/day) and toxic levels (> 400 μg/day for adults) (Floor and Román-Ross 2012). Se has a focal role in cancer development (Floor and Román-Ross 2012; Patrick 2004). There is scarce information on the process in which Se impacts from volcanoes affect populations living in the vicinity of volcanos. Some studies indicate an enhanced cancer risk in volcanic areas, i.e., increased frequency rates of thyroid cancer (Duntas and Doumas 2009; Pellegriti et al. 2009).

U (Fig. 5, Tables 2, 3, and 4), similarly to Cr, showed higher similar levels ($KW = 98.53$, $p < 0.001$, see letter a) after the volcano event i.e., 0.104 μg g^{-1} in 2011 and 0.101 μg g^{-1} in 2012 respectively (see letter a) compared with 2006

Table 2 Descriptive statistics of the elements' concentrations (μg/g d.w.) in native lichens collected in Tierra del Fuego (Patagonia) after 3 months of the volcanic eruption (September 2011)

Elements 2011	Min	Q1	Median	Mean	Q3	Max	SD
As	0.09	0.37	0.55	0.86	0.97	6.06	0.94
Ba	5.70	19.12	27.10	28.70	37.25	70.00	13.78
Br	4.81	9.98	13.95	15.46	19.83	39.86	7.67
Ca	659	2442	4369	5617	7446	23,403	4483
Ce	0.18	0.76	1.59	1.94	2.56	11.59	1.75
Co	0.06	0.17	0.34	0.52	0.58	3.15	0.56
Cr	0.70	2.56	4.95	7.11	9.46	35.2	6.79
Cs	0.014	0.047	0.095	0.110	0.150	0.440	0.09
Eu	0.004	0.019	0.036	0.043	0.053	0.250	0.040
Fe	53	249	639	962	1147	7466	1181
Hf	0.01	0.05	0.09	0.11	0.12	0.72	0.11
K	956	3167	3844	4194	4815	17,900	2124
La	0.049	0.284	0.682	0.823	1.032	5.329	0.82
Lu	0.002	0.007	0.013	0.018	0.020	0.110	0.020
Na	298	871	1367	1731	2170	9364	1265
Rb	0.89	1.84	3.23	3.67	4.47	11.90	2.19
Sb	0.009	0.024	0.042	0.089	0.097	0.810	0.130
Sc	0.021	0.134	0.326	0.413	0.508	2.332	0.390
Se	0.135	0.250	0.331	0.343	0.416	0.756	0.120
Sm	0.011	0.073	0.155	0.203	0.265	1.304	0.190
Ta	0.004	0.016	0.021	0.028	0.031	0.145	0.024
Tb	0.012	0.025	0.042	0.051	0.059	0.226	0.040
Th	0.020	0.081	0.172	0.236	0.299	1.824	0.260
U	0.040	0.073	0.104	0.132	0.154	0.480	0.090
Yb	0.001	0.041	0.071	0.099	0.121	0.636	0.10
Zn	13.7	26.9	31.9	33.9	37.7	89.1	13.01

baseline levels (0.03 μg g^{-1}, letter b). This corresponds to an increase of uranium by a CF of about 3.4 after the volcano event. These results, obtained from the forested areas, match those obtained for transplants collected in the northern areas of TdF, which showed an increase by a CF of 4 for U (Conti et al. 2016). In fact, volcanic ash samples collected after the volcano event from direct fallout showed high levels of U (i.e., 2.51–3.06 μg g^{-1}) and Cr (2.24–9.10 μg g^{-1}) (Daga et al. 2014). Regarding mechanisms of bioaccumulation, it has been shown that melanin in lichens has a relevant role showing high U bioaccumulation capacity (McLean et al., 1998). The authors report that melanization in *Thuarea involuta* is an adaptive response aiming to protect the ascospores (the sexual reproductive bodies) from the toxic effects of the uranium.

Zn (Fig. 5, Tables 2, 3, and 4) showed higher levels in the 2006 sampling campaign (i.e., 41.1 μg g^{-1}, see letter a) than those obtained after the volcano event (letter b), i.e., 31.9 and 30.6 μg g^{-1} in 2011 and 2012 respectively (KW = 14.61, $p < 0.001$) which resulted in being similar indicating a constant airborne Zn deposition over time. In general, the median Zn levels detected in lichens from the forested areas of Tierra del Fuego in this study were lower, by a factor 2–3, than those detected in the transplants collected in the north of TdF (Conti et al. 2016). Lubrication oils and brake pads are known sources of Zn from vehicle emissions. However, considering the very low traffic levels in TdF (Pino et al. 2010), we can attribute the Zn content in the biomonitor mainly to atmospheric deposition, including volcanic ashes.

Comparing our results in lichens collected in September 2011 with those reported for double washed native samples of *Usnea* in Antarctica (Bubach et al. 2016, and assuming data in this work are reported as μg g^{-1} d.w.), the ranges of several metal concentrations in the present survey are higher (i.e., 956–17,900 μg g^{-1} for K; 298–9364 μg g^{-1} for Na; 13.7–89.1 μg g^{-1} for Zn) with respect to those collected in Antarctica (i.e., 1380–3120 μg g^{-1} for K; 229–941 μg g^{-1} for Na; 0.51–6.8 μg g^{-1} for Zn). However, caution is needed in comparing results with different sampling strategies (unwashed vs. washed lichens, as above reported).

Bioaccumulation trends

Going deeper, we have tested element bioaccumulation in lichens between the sampling campaigns after the volcano

Table 3 Descriptive statistics of the elements' concentrations (μg/g d.w.) in native lichens collected in Tierra del Fuego (Patagonia) after 15 months of the volcanic eruption (September 2012)

Elements 2012	Min	Q1	Median	Mean	Q3	Max	SD
As	0.10	0.24	0.46	0.72	0.98	3.24	0.63
Ba	4.80	14.55	22.0	23.87	27.90	73.00	12.53
Br	2.61	8.00	11.87	14.25	17.86	37.31	8.15
Ca	487	2090	4000	5857	7625	26,000	5123
Ce	0.20	0.62	1.26	1.76	2.75	7.30	1.50
Co	0.06	0.14	0.26	0.42	0.56	1.78	0.40
Cr	0.23	1.08	2.28	3.39	4.60	21.58	3.39
Cs	0.014	0.039	0.084	0.102	0.145	0.360	0.080
Eu	0.004	0.013	0.029	0.038	0.055	0.168	0.030
Fe	53	181	516	785	1082	3549	765
Hf	0.01	0.03	0.06	0.09	0.13	0.48	0.83
K	229	1870	2900	3070	4250	8000	1823.9
La	0.054	0.232	0.538	0.754	1.122	3.482	0.690
Lu	0.002	0.006	0.009	0.016	0.023	0.068	0.013
Na	297	704	1084	1166	1442	3480	610.8
Rb	0.57	1.69	2.73	3.17	4.00	15.40	2.13
Sb	0.006	0.018	0.033	0.069	0.990	0.570	0.090
Sc	0.029	0.122	0.306	0.373	0.495	1.388	0.320
Se	0.147	0.248	0.333	0.373	0.424	1.760	0.190
Sm	0.016	0.057	0.131	0.187	0.272	0.804	0.170
Ta	0.004	0.013	0.018	0.023	0.029	0.089	0.020
Tb	0.009	0.023	0.038	0.047	0.069	0.135	0.030
Th	0.021	0.065	0.139	0.211	0.300	1.054	0.190
U	0.033	0.067	0.101	0.114	0.144	0.334	0.060
Yb	0.009	0.032	0.062	0.096	0.127	0.429	0.08
Zn	14.0	24.3	30.6	34.3	38.5	143.6	17.4

event (2011 ➔ 2012). The main result is that 20 out of 26 studied elements (i.e., As, Br, Ca, Ce, Co, Cs, Eu, Fe, La, Lu, Sb, Sc, Se, Sm, Ta, Tb, Th, U, Yb, and Zn) showed no significant pattern of bioaccumulation (MW = n.s.) and remained quite constant in the considered period.

Table 4 Descriptive statistics for the baseline elements' bioaccumulation (μg/g d.w.) in *U. barbata* samples collected in 2006 before the volcanic eruption in Tierra del Fuego region (Patagonia)

Elements 2006	Min	Q1	Median	Mean	Q3	Max	SD
As	< 0.09	0.17	0.50	0.66	1.01	2.78	0.61
Ba	2.19	10.19	15.38	21.81	27.23	109.62	20.3
Ca	405	1278	2156	3562	4484	20,726	3610.2
Co	0.03	0.22	0.30	0.41	0.52	1.42	0.29
Cr	0.08	0.45	0.67	0.84	1.12	2.64	0.57
Cs	0.01	0.03	0.06	0.07	0.09	0.29	0.06
Fe	17	244	714	1222	1593	6073	1444
K	882	1734	3473	4664	6128	16,049	3523.5
Na	99	395	768	806	1036	3273	555
Sb	0.008	0.015	0.03	0.06	0.09	0.3	0.07
Se	0.02	0.32	0.53	0.66	0.96	2.16	0.46
U	0.01	0.01	0.03	0.03	0.04	0.18	0.03
Zn	3.8	28.2	41.1	48.3	57.9	280.2	37.9

On the other hand, significant differences (2011 ➔ 2012) were obtained for Ba, Cr, K, and Na (discussed in the "Impact of the volcanic eruption on the regional atmospheric deposition" section). Moreover, we detected significant differences also for Hf (MW = 11,164, $p = 0.04$) and Rb (MW = 11,703, $p = 0.02$). These elements showed a decreasing bioaccumulation trend between 2011 and 2012 sampling campaigns. In particular, the median levels of these elements decreased as follows (2011 ➔ 2012): − 18.8% for Ba; − 53.9% for Cr, − 33.3% for Hf, − 24.6% for K, − 20.6% for Na, and − 15.6% for Rb (see Tables 2 and 3).

The aerosol phase of the airborne plume usually contains trace elements. Many elements, i.e., halogens, sulfur, and others, can impact both areas near the volcano and distant geographical areas, such as in this study (the distance of our sampling sites to the volcano is 1700 km) (Bubach et al. 2012, 2014; Mather et al. 2012; Moune et al. 2010; Bagnato et al. 2013). In particular, volcanic gasses contain several elements such as Na and K, and a lesser quantity of some alkalis like Li, Cs, and Rb, and halogens, i.e., F, Br, and I (Fegley Jr and Zolotov 2000; Schaefer and Fegley Jr 2005). It is worth noting that the entire island was covered by tephras (volcanic ashes) several times in 2011.

Br is a halogen emitted by volcanic eruptions and typically relates to petrochemical industries, Chlor-alkali plants, and traffic. Measuring volcanic Br emissions is an extremely complex matter (Mather 2015). We detected a similar median concentration of Br in lichens of 13.95 and 11.87 μg/g in 2011 and 2012, respectively. Furthermore, Br is also involved in the ozone depletion process (Bubach et al. 2012). However, as already reported, the traffic frequency is very low in TdF, and there is no heavy industry in the area, suggesting the atmospheric deposition from the volcano as the primary source of some elements such as Ca, Na, K, and Br.

Volcanic ash could pose a hazard to people living in the vicinity; for instance, the ocular surface can be severely affected as it is constantly exposed to environmental particles (Tesone et al. 2018).

In this study, the natural contamination by tephras is reflected by lichens more clearly in the 2011 sampling campaign, where the median levels of Ba, Cr, Hf, K, Na, and Rb were significantly higher than those of the 2012 campaign.

As already reported above, lichens usually contain huge levels of macroelements (Conti et al. 2012). We found that Ca, K, and Na (i.e., 4369, 3844, and 1367 μg g^{-1}, respectively) were the most accumulated elements in 2011, while the baseline (2006) median levels were lower, i.e., 2156, 3473, and 768 μg g^{-1} for Ca, K, and Na, respectively. This corresponds to an increase of 50.6%, 9.65%, and 43.8% for Ca, K, and Na, from 2006 ➔ 2011, respectively. These higher levels of macroelements detected in 2011 can be mostly associated with the volcanic ashes' deposition. A similar trend was obtained for these macroelements in the northern areas of TdF studied by using transplants (Conti et al. 2016).

The correlation between cationic concentrations in lichens is employed as an index of acid precipitation. The concentration of macroelements in lichens can be controlled by the acidity of atmospheric rainfall. K has an important role connected with lichen integrity (Hyvärinen and Crittenden 1996), i.e., it has reported a positive correlation between chlorophyll integrity and K concentrations. Moreover, cell membrane damage is related to the loss of K (see Garty et al. 1998a, b; Conti and Cecchetti 2001).

Rare earth elements (REEs) are present in geological environments, with endogenous deposits resulting from processes inside the Earth's crust, and exogenous deposits, built during weathering and/or sedimentary processes (Paulick and Machacek 2017). The REE bioaccumulation patterns in lichens can give information on the origin of elements associated with bulk precipitation or local lithology (Chiarenzelli et al. 2001; Brioschi et al. 2013; Agnan et al. 2015).

The REEs analyzed in lichens (Ce, Eu, La, Lu, Sc, Sm, Tb, and Yb) showed no significant bioaccumulation levels between 2011 and 2012 sampling campaigns. This confirms previous findings we obtained in the northern desertic areas of TdF employing lichen transplants (Conti et al. 2016), where REEs showed no significant differences. This response seems to be strongly associated with higher lithogenic inputs than those determined from volcanic ashes. The strong lithologic influence of the REE bioaccumulation in lichens has been previously reported by studies conducted in Córdoba (Argentina) and in the southwest of France (Pignata et al. 2007; Agnan et al. 2014).

Regarding EFs and using the Earth's crust as a reference, nine elements (As, Ba, Br, Ca, K, Na, Sb, Se, and Zn) presented mean EF values above 5. Br and Se showed very high EF values in the 2011 and 2012 sampling campaigns (Supplementary Material Figs. S1–S2).

However, it should be considered that Br can also originate from marine aerosols, as reported by Vieira et al. (2004). Recalculation of Br EFs using Na and seawater (Goldberg 1963) as reference rendered mean EFs of 1.67 and 2.05 for 2011 and 2012 respectively, thus indicating an important contribution of marine aerosol for this element.

Zn, As, and Sb can be released from the magma due to their aptness to form stable volatile compounds with strong ligands (i.e., Cl, F, and S) (Bagnato et al. 2013). These results further support our findings connected with the lichen bioaccumulation patterns reported above.

For each of the nine elements mentioned above, and to assess the variation of EFs within a sampling campaign, a modification of the scale proposed by Sutherland (2000) was adopted: $EF < 5$ minimal enrichment; $5 < EF < 20$ moderate to significant enrichment; $20 < EF < 40$ very high enrichment; and $EF > 40$ extremely high enrichment. Undetermined (undetected or missing) values were considered another class. Table 5 shows the results of this study. For As, Sb, and Zn,

Table 5 Enrichment factors (in %) calculated using Mason's crustal values and Fe as references

	2011 campaign—enrichment factors (Mason's crustal and Fe as references)								
	As	Ba	Br	Ca	K	Na	Sb	Se	Zn
	%	%	%	%	%	%	%	%	%
EF < 5 minimal enrichment		52.0		28.7	10.7	58.0	0.7		0.7
5 < EF < 20 moderate to significant enrichment	26.7	22.0		41.3	28.0	26.7	52.0		20.0
20 < EF < 40 very high enrichment	49.3	3.3	1.3	12.7	6.7	8.7	27.3		34.7
EF > 40 Extremely high enrichment	13.3	4.0	98.7	14.7	14.0	6.7	11.3	99.3	44.0
Undetermined	10.7	18.7		2.7	40.7		8.7	0.7	0.7
	2011 campaign—enrichment factors (Mason's crustal and Fe as references)								
	As	Ba	Br	Ca	K	Na	Sb	Se	Zn
	%	%	%	%	%	%	%	%	%
EF < 5 minimal enrichment		58.0		22.7	18.7	58.0			
5 < EF < 20 moderate to significant enrichment	24.7	22.0		48.0	30.7	30.7	50.7		17.3
20 < EF < 40 very high enrichment	54.0	6.0	2.0	11.3	8.7	8.7	32.7		31.3
EF > 40 Extremely high enrichment	14.0	4.0	98.0	18.0	10.7	2.7	14.0	96.0	49.3
Undetermined	7.3	10.0			31.3		2.7	4.0	2.0

for the 2011 campaign, nearly all EF results were above 5. As presented, about 49% are of very high enrichment, while for Sb and Zn, the highest percentages corresponded to moderate to significant (52%) and extremely high enrichment (44%), respectively. Results for the 2012 campaign were like those for 2011 one. Information about the other determined elements is in Table 5.

The forested areas in central south TdF showed elevated deposition levels of airborne PM naturally produced. This finding confirms our previous survey conducted in the northern areas of TdF in which high deposition levels of natural PM have been reported. Numerous studies report that volcanic eruptions can generate emissions in the atmosphere of high levels of PM, yielding a possible impact on respiratory and cardiovascular morbidities and causing mortality. Nevertheless, the assessment of potential adverse health effects generated by a volcanic event is a matter of debate (Tesche et al. 2012).

However, more research is needed (Getty et al. 1999) to understand the elements better mostly linked with natural origin, i.e., soil erosion and volcanic ashes, and those most associated with anthropogenic origin.

Conclusions

This long-term survey (6 years), through the application of the MBS conceptual model, allowed the generation of valuable results related to the dynamic processes of air pollution, secondary to a natural event, quantifying temporal and spatial aspects of the environmental distribution of twenty-six elements including REEs. The study, conducted in the forested areas of TdF (southern Patagonia), contributes to the knowledge of the natural spatial and temporal dynamics of a number of chemical components of PM released in a volcanic eruption (started in June 2011), as well as of their impacts on distant ecosystems in three sampling campaigns (2006: baseline; ➔ 2011–2012: 3 and 15 months after the volcano event, respectively).

The natural contamination by tephras is reflected by lichens more evidently in 2011, where the median levels of Ba, Cr, Hf, K, Na, and Rb were significantly higher than those of the 2012 sampling campaign.

Lichens, as expected, showed high levels of macroelements. Ca, K, and Na were the most accumulated elements in the 2011 sampling campaign. These higher levels of macroelements detected in 2011 can be generally associated with the volcanic ashes' deposition.

In summary, several elements showed higher significant levels in the 2011 campaign (i.e., Ba, Cr, Na, Ca, Cs, and U) compared with the baseline (2006), while Se and Zn levels decreased in 2011 with respect to the baseline levels (2006). Using Earth's crust as reference, nine elements (As, Ba, Br, Ca, K, Na, Sb, Se, and Zn) presented mean enrichment factor values above 5, but recalculation for Br with Na and seawater as a reference gave means of 1.67 and 2.05 for 2011 and 2012 respectively.

In conclusion, we propose here to conceptualize the wide set of biomonitoring knowledge endowment as an open and evolutionary endowment of information variety supporting environmental management. This approach consented to underline better the good agreement we generally obtained between the use of native lichens and the transplant method.

Furthermore, the usefulness of lichens (*Usnea barbata*) as test species for direct biomonitoring oriented kinetic studies of environmental (terrestrial) variables in areas characterized by

a low human impact is confirmed. Eventually, from our results, we confirm that TdF is not an actual pristine environment as earlier supposed.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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