

Temporal fluctuations of mineral concentrations as related to the physiological status of the lichen *Ramalina lacera* (With.) J.R. Laund.

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ABSTRACT

The present review deals with alterations in Ca, K, Mg, Na, and P content and chlorophyll integrity of the epiphytic fruticose lichen *Ramalina lacera* in a forested rural area in Israel over an extended period. In the years 1978–2002, Ca was found to accumulate in significant amounts whereas the P content decreased. The K content did not change significantly in this period. The Mg and Na content measured in the years 1993–2002 did not show a clear pattern of change, either. The accumulation of Ca coincided with a significant increase of dust storms, originating in the Sahara Desert, in terms of dust-stormy days. The source of the above-mentioned elements is discussed.

Keywords: biomonitoring, calcium, chlorophyll, lichen, Saharan dust

INTRODUCTION

Lichens are perennial slow-growing associations of fungi (mycobionts) and green algae or cyanobacteria (photobionts). This symbiotic association forms a common thallus, without roots or waxy cuticles, which depends entirely on an atmospheric input of mineral nutrients. The concentration of mineral elements in lichen thalli correlates directly with environmental levels of these elements (Bari et al., 2001; Bergamaschi et al., 2004). This feature of lichens, combined with their extraordinary capability to grow in a large geographical range and to accumulate mineral elements far above their need, ranks them among the best bioindicators of air pollution (see reviews, Bargagli, 1998; Garty, 2001; Wolterbeek et al., 2003).

The present review examined temporal alterations in several mineral elements, Ca, K, Mg, Na, and P, in a

lichen during a period of 10–24 years. These non-toxic nutrient elements derive, at least partly, from geochemical sources. This review was to detect the potential impact of a changing environment in terms of accumulation rates of the above-mentioned elements in *Ramalina lacera* (With.) J.R. Laund, growing in a forested area for one or two decades.

An additional focus of interest was the physiological status of lichen thalli over the years in this rural site. Data referring to changes in physiological parameters, obtained in the years 1981–2002, were analyzed to determine whether the level of chlorophyll integrity in the forested area in 2002 was similar to the status observed two decades earlier.

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MATERIALS AND METHODS

Study area, collection, and treatment

The study focused on a rural site, the HaZorea Forest in Ramot Menashe Hills, NE Israel. The Ramot Menashe region (32°37'N 35°E) is located 30 km southeast of the city of Haifa. The topography is characterized by low hills (elevation <200 m asl) formed by Eocene chalk outcrops (Dufour-Dror, 2007). The soils are mainly shallow Rendzina, either light brown or grey (Singer and Ravikovitch, 1980). The climate is typically Mediterranean. The annual rainfall average is 650 mm and the Mediterranean bio-climate is sub-humid and hot, with a remarkable long dry season lasting 7 months (Dufour-Dror and Ertas, 2004; Dufour-Dror, 2007). It is regarded as a clean site (Garty et al., 2003).

In August 2002, 300 thalli were collected in several scattered sites in the forest and transported to the laboratory. The thalli were detached from the substrate and rinsed immediately with double-distilled water at a temperature of 20 °C, to eliminate dust. The rinsing procedure was repeated three times for 5 s each. The rinsing procedure was carried out in this manner to minimize the loss of water-soluble elements, i.e., K, Mg (Buck and Brown, 1979), and Na, known to occur. Because of the Israeli climate, avoidance of rinsing may leave the thallus covered with a thick layer of

dust and yield, as a result, irrelevant chemical and physiological data.

Determination of elemental content

To measure the Ca, K, Mg, Na, and P content of the lichen, subsamples of 1–2 g of rinsed and air-dried thalli were ground with liquid nitrogen to make a powder. This powder was dried for 24 h at 105 °C. Subsamples of 250 mg were digested in 10 ml of concentrated HNO₃ in test tubes of 50 ml in a heating block for a duration of 8 h at a temperature of 120 °C. The elemental content was determined by inductively coupled plasma (ICP)—atomic emission spectrometry (AES) by the Spectro-flame ICP (Spectro, Kleve, Germany). The reference material used to check the accuracy of our measurements was the IAEA–336 lichen certified reference material supplied by the International Atomic Energy Agency, Vienna, Austria. The reference sheet was updated in June 1999.

Assessment of physiological status

The vitality of the *R. lacera* in the HaZorea forest was assessed by testing the integrity of the photobiont chlorophyll. For this purpose we applied the method of Ronen and Galun (1984), by means of a Novaspec II spectrometer (Pharmacia, LKB, Biochrom Ltd., Cambridge, UK).

Table 1

Mean ± SD values of Ca, K, and P content of *Ramalina lacera* collected in HaZorea Forest in the years 1978–2002 and the values of Mg and Na in thalli of the lichen collected in this site in the period March 1993–August 2002

| Collection date | Ca | K | Mg | Na | P | Reference |
|-----------------|---------------------------|-------------------------|------------------------|------------------------|-------------------------|--|
| May 1978 | 6300 | 2600 | – | – | 2700 | Fuchs and Garty, 1983 |
| December 1978 | 6200 | 2500 | – | – | 2800 | Fuchs and Garty, 1983 |
| February 1979 | 6500 | 2500 | – | – | 2800 | Fuchs and Garty, 1983 |
| March 1980 | 6800 | 2500 | – | – | 2700 | Fuchs and Garty, 1983 |
| July 1981 | 9190 ± 1473 | 2702 ± 253 | – | – | 3927 ± 1043 | Garty et al., 1985 |
| March 1993 | 10795 ± 4096 | – | 884 ± 135 | 528 ± 76 | 1574 ± 529 | Garty and Kloog, unpublished |
| June 1993 | 7873 ± 2110 | – | 1087 ± 153 | 753 ± 194 | – | Garty et al., 1997a |
| January 1994 | 13256 ± 1848 | 2618 ± 359 | 830 ± 287 | 507 ± 185 | 1699 ± 221 | Garty and Kloog, unpublished |
| February 1994 | 9119 ± 2042 ^a | 2366 ± 208 ^b | 922 ± 134 ^b | 537 ± 148 ^a | 1279 ± 272 ^b | (a) Garty and Kloog, unpublished (b) Garty et al., 1997d |
| June 1994 | 12562 ± 1516 | 2834 ± 284 | 873 ± 55 | 1035 ± 359 | 1447 ± 295 | Garty and Kloog, unpublished |
| November 1994 | 15754 ± 2817 | 2163 ± 400 | 777 ± 143 | 493 ± 140 | 1183 ± 395 | Garty and Kloog, unpublished |
| August 1995 | 16758 ± 2190 ^c | 2232 ± 344 ^d | 848 ± 112 ^c | 736 ± 39 ^c | 996 ± 310 ^d | (c) Garty et al., 2002a (d) Garty et al., 1997b (e) Garty and Wolfson, unpublished |
| June 1996 | 23383 ± 4913 | – | – | – | – | Garty et al., 2002a |
| May 1997 | 34310 ± 3522 | 2740 ± 237 | 941 ± 68 | 437 ± 46 | 1828 ± 215 | Garty et al., 2001a |
| November 1997 | 19161 ± 1248 ^f | 2130 ± 184 ^g | 731 ± 46 ^f | 262 ± 41 ^f | 1008 ± 113 ^f | (f) Garty and Weissman, unpublished (g) Garty et al., 2000 |
| November 1998 | – | 2239 ± 196 | – | – | – | Garty et al., 2001b |
| January 2001 | 25257 ± 3624 | 2299 ± 254 | 835 ± 104 | 228 ± 25 | 1192 ± 244 | Garty et al., 2003 |
| August 2002 | 36608 ± 7563 | 2588 ± 222 | 1262 ± 122 | 447 ± 40 | 1025 ± 70 | This study |

Values are in µg g⁻¹ on dry weight basis.

Statistical analysis

The results of the chemical and physiological analyses were evaluated using the Pearson correlation test to analyze the obtained data versus date of lichen collection in the years 1978–2002.

RESULTS

Elemental content, integrity of chlorophyll, and correlation of parameters with date of collection for *R. lacera*

Data of elemental content are presented in Table 1. Thalli of *R. lacera* contained large amounts of Ca, K, Mg, Na, and P relative to the concentrations of most of the trace elements detected in this lichen in the same location in January 2001 (Garty et al., 2003). The comparable values for B, Ba, Co, Cr, Cu, Mn, Ni, Pb, Sn, Sr, Ti, V, and Zn were 5.0 ± 0.7 , 14.5 ± 2.1 , 0.46 ± 0.07 , 4.6 ± 1.5 , 7.1 ± 4.0 , 21.8 ± 2.8 , 4.0 ± 0.9 , 7.3 ± 1.0 , 0.78 ± 0.30 , 29.8 ± 5.2 , 94 ± 13 , 4.9 ± 0.6 , and $34.6 \pm 2.2 \mu\text{g g}^{-1}$ on dry weight basis, respectively. Selected data for Ca and K in other epiphytic lichen species in different countries in the Mediterranean basin are presented for comparison with *R. lacera* content in Table 4, and for Mg and Na in Table 5. A comparison of Ca-content of *R. lacera* collected in HaZorea in May 1978 (Fuchs and Garty, 1983) and in August 2002 (Table 1, present study), shows a dramatic increase in Ca content. The Pearson correlation for Ca content versus date of lichen collection, performed for Ca content of *R. lacera* in HaZorea over 24 years, shows a significant ($r = 0.76$; $p < 0.01$) increase. The elemental content of K, Mg, Na, and P, on the other hand, did not show a similar pattern. K, Mg, and Na values showed a slight fluctuation along two decades without a distinctive trend ($r = 0.043$; $p = 0.33$; $r = 0.36$; $p = 0.28$; $r = -0.57$; $p = 0.06$, respectively). P values, however, showed a significant decrease ($r = -0.88$; $p = 0.000$) in these years. The Pearson correlation test performed for Ca content versus P content in the years 1978–2002 shows a significant negative correlation ($r = -0.55$; $p = 0.033$). The Pearson correlation test (OD 435 nm/OD 415 nm versus date of lichen collection) indicated (Table 2) a stable ratio ($r = 0.026$; $p = 0.89$) in *R. lacera* in the HaZorea Forest over 20 years and more.

DISCUSSION

The elemental content of *R. lacera*

The present study, which applied the lichen *R. lacera* as a bioindicator of the airborne physiologically important chemical elements Ca, K, Mg, Na, and P (Nieboer and

Table 2

Mean \pm SD of the OD 435 nm/OD 415 nm ratio expressing chlorophyll status in thalli of *Ramalina lacera* collected in HaZorea Forest in the years 1981–2002

| Collection date | | OD 435 nm/ OD 415 nm | References |
|-----------------|------|-------------------------|-------------------------------|
| April | 1981 | 1.42 ± 0.03 | Garty et al., 1985 |
| July | 1981 | 1.42 ± 0.03 | Garty et al., 1985 |
| December | 1982 | 1.43 ± 0.05 | Ronen et al., 1985 |
| November | 1983 | 1.37 ± 0.04 | Ronen, 1986 |
| December | 1983 | 1.43 ± 0.03 | Ronen, 1986 |
| January | 1984 | 1.46 ± 0.01 | Ronen, 1986 |
| February | 1984 | 1.38 ± 0.09 | Ronen, 1986 |
| March | 1984 | 1.39 ± 0.07 | Ronen, 1986 |
| May | 1984 | 1.40 ± 0.10 | Ronen, 1986 |
| June | 1984 | 1.46 ± 0.03 | Ronen, 1986 |
| July | 1984 | 1.44 ± 0.04 | Kardish et al., 1987 |
| August | 1984 | 1.45 ± 0.06 | Ronen, 1986 |
| January | 1985 | 1.41 ± 0.04 | Kardish et al., 1987 |
| March | 1985 | 1.40 ± 0.02 | Kardish et al., 1987 |
| July | 1985 | 1.44 ± 0.04 | Kardish et al., 1987 |
| June | 1989 | 1.45 ± 0.05 | Garty and Karary, unpublished |
| September | 1989 | 1.45 ± 0.05 | Garty et al., 1993a |
| December | 1989 | 1.44 ± 0.04 | Garty et al., 1993a |
| February | 1990 | 1.45 ± 0.02 | Garty et al., 1993a |
| April | 1990 | 1.52 ± 0.02 | Garty et al., 1993a |
| June | 1990 | 1.42 ± 0.02 | Garty et al., 1993a |
| March | 1993 | 1.47 ± 0.02 | Garty et al., 1997a |
| June | 1993 | 1.43 ± 0.02 | Garty et al., 1997a |
| January | 1994 | 1.42 ± 0.02 | Garty et al., 1997c |
| February | 1994 | 1.48 ± 0.01 | Garty and Kloog, unpublished |
| June | 1994 | 1.44 ± 0.14 | Garty and Kloog, unpublished |
| November | 1994 | 1.42 ± 0.03 | Garty et al., 1998 |
| August | 1995 | 1.38 ± 0.03 | Garty et al., 1997b |
| May | 1997 | 1.43 ± 0.02 | Garty et al., 2001a |
| November | 1997 | 1.40 ± 0.09 | Garty et al., 2000 |
| November | 1998 | 1.39 ± 0.05 | Garty et al., 2001b |
| August | 2002 | 1.39 ± 0.02 | This study |

Richardson, 1980; Branquinho and Brown, 1994) in a forested area, raised the question of the possible source of these elements in an unpolluted region. The dry deposition of dust is the potential source of these major elements. Previous studies of the impact of dust on lichens revealed that in an area exposed to intensive anthropogenic activity, dust may derive from metal smelters (see review, Garty, 2001; Otnyukova, 2007), oil shale fueled power plants (Jalkanen et al., 2000), cement factories (Jalkanen et al., 2000; Branquinho et al., 2008), sandstone quarries (Loppi and Pirintzos, 2000), limestone quarries (Zaharopolou et al., 1993; Loppi and Pirintzos, 2000; Branquinho et al., 2008), sand processing plants,

truck traffic (Dias da Cunha et al., 2004), and unpaved roads (Farmer, 1993; Branquinho et al., 2008).

In Israel, dominant anthropogenic sources are producers of fertilizers; quarries where carbonatic rocks such as limestone and dolomite are used to produce building stones, gravel, and cement; construction sites of residential areas; and roads emitting Ca, Mg, Na, and P. Under anthropogenic pollution, lichens tend to undergo a process of replacement of macronutrients by pollutants. The best example of this process in lichens is the decrease of K related to cell membrane damage following pollution by SO₂ and heavy metals (see review, Garty, 2001). Other research articles indicated K loss from lichens following exposure to Cu (Cabral, 2003), H₂AsO₄ (Mrak et al., 2007), HNO₃ gas (Riddell et al., 2008), urban atmosphere (Adamo et al., 2003; Tretiach et al., 2007), industry (Garty et al., 2002a,b; Williamson et al., 2004), and evaporation ponds containing organic liquids (Garty et al., 2002b).

On the other hand, the K content of lichens may increase due to exposure to alkaline coal ash (Walker et al., 2003) or to K- and P-containing fertilizers in a shipping terminal (Garty et al., 1998). The slight fluctuation of K content of *R. lacera* collected in HaZorea in the period May 1978–August 2002, though surprising, is in accordance with findings of Ra et al. (2005) who could not detect a definite seasonal change of concentrations of K, Ca, Mg, and Na in the thalli of *Platismatia glauca* in the U.S. Pacific Northwest.

The assumption that soil dust contributes largely to the accumulation of fine particles on top of exposed lichens in urban areas, is supported by a significant correlation between mineral elements such as Al, Ca, Cu, Fe, K, Mg, and Mn (Adamo et al., 2008b). The present study, however, performed in a rural area, suggests that the major elements detected in the lichen *R. lacera* are also of a natural source. In the Mediterranean region, a significant source of dust is the Sahara Desert (Meloni et al., 2007). Dust plumes originating in the Sahara Desert contribute significantly to the atmospheric aerosol mass in episodes of long-range transport. As a result, an enhanced deposition of crustal material occurs over large areas at a great distance from the source (Eleftheriadis et al., 1999). Several reports characterized the geochemical composition of Saharan dust collected in peri-Saharan areas, SW of Morocco (Khiri et al., 2004), and in Europe (e.g., Eleftheriadis et al., 1999; Kandler et al., 2007). Studies of the mineral composition of dust from the Sahara and from other deserts in Africa and the Eastern Mediterranean found that the greater part of the minerals identified in dust contain Ca. The most ubiquitous minerals are calcite (CaCO₃), dolomite (CaMg(CO₃)₂), and gypsum (CaSO₄ · 2H₂O) (Foner

and Ganor, 1992; Jiries et al., 2002; Krueger et al., 2004). Analyses of the chemical composition of aerosols settling in Israel via dust storms determined that Ca can reach 128 ± 36 mg g⁻¹, K—8.6 ± 3.58 mg g⁻¹, Mg—23.4 ± 6.8 mg g⁻¹, Na—4.9 ± 1.35 mg g⁻¹, and P—3.16 ± 1.95 mg g⁻¹ (Ganor et al., 1991). The high Ca content of aerosols listed above may explain, to a certain extent, the large amount of Ca in *R. lacera* detected in the present study. Wet deposition is probably an additional source of the Ca detected in the lichen thallus. Calcium is an important constituent of continental origin in rain in the Eastern Mediterranean, as reported for Israel (e.g., Singer, 1994; Herut et al., 2000) and for Jordan (e.g., Jiries, 2001; Al-Momani, 2003). The high Ca content of the lichen from HaZorea reflects, in addition to dust traveling long distances, a notable amount of wind-blown dust particles containing CaCO₃ derived from local soil deposited on limestone and chalk rocks. This is consistent with the presence of these rocks and with the Ca-rich soil in the HaZorea region. Local soil/dust cannot, however, account for the gradual trend of increase of Ca content between 1978 and 2002 (Table 1). The factor that should be added is the increasing number of dust storms in the last four decades. According to Ganor et al. (2007), the number of days with dust events in Israel (measured in Tel Aviv), per year, has increased (1958–2006) from 5 days in 1958 to 30 days in 2006. According to the same reference, dust events are most common in March and April, and the presence of dust increases the probability of rain.

A retrospective examination of the Ca content of another *Ramalina* species, *R. maciformis* collected in an unpolluted site in the Negev Desert in the years 1990–1999 (Table 3), revealed a rather stable Ca content (ca. 60,000 µg g⁻¹) without a distinct increase over a decade. This observation contradicts, apparently, our conclusions with regard to the gradual accumulation of Ca in *R. lacera* and its association with the gradual

Table 3

Mean ± SD values of Ca content in *R. maciformis* collected in a control site (Tellalim) in the Negev Desert in the years 1990–1999

| Collection date | Ca | References |
|-----------------|---------------|------------------------------|
| December 1990 | 64233 ± 7001 | Garty et al., 1996 |
| February 1992 | 60098 ± 11055 | Garty et al., 1996 |
| March 1993 | 57106 ± 7776 | Garty et al., 2007 |
| June 1993 | 57885 ± 4389 | Garty et al., 2007 |
| November 1993 | 60566 ± 4093 | Garty et al., 2007 |
| April 1998 | 60529 ± 6753 | Garty et al., 2002b |
| November 1999 | 61330 ± 5564 | Garty and Levin, unpublished |

Values are in µg g⁻¹ on dry weight basis.

increase of the number of dust storms. This apparent discrepancy is accounted for by the fact that the *R. lacera* grows in HaZorea on carob trees planted by the Jewish National Fund near the kibbutz (in 1938) about 70 years ago whereas the epilithic *R. maciformis* in the Negev is probably a few hundred years old. If indeed this is the case, the thalli of the latter species are presumed to be “saturated” by Ca ($60,000 \mu\text{g g}^{-1}$) and the continuous supply of airborne Ca in the desert with the increasing number of dust storms may then not leave its mark. The maximal amount of Ca potentially accumulating in the epiphytic *R. lacera* cannot be predicted reasonably at this stage.

Although Ca has no toxic effect and may be considered a “normal” ecological factor (van Dobben et al., 2001), following the track of its accumulation pattern in lichens yields important information about the increase of the annual number of dust storms in arid areas, pointing to a pattern of climatic change, i.e., the increase of warming and desertification.

The stable OD 435 nm/OD 415 nm ratio in *R. lacera* in the HaZorea Forest over 20 years and more in spite of the accumulation of Ca, demonstrated in the present study, is surprising. The greater exposure to dust will, in some cases, cause damage to the photobiont chlorophyll, evidenced by an increased phaeophytin percentage. This

phenomenon was demonstrated by an analysis of thalli of *Physcia adscendens* collected near a limestone quarry in Greece (Zahropoulou et al., 1993). We did not find evidence of this phenomenon in the present study. Table 2, which refers also to seasonal change, does not show a clear pattern of OD 435 nm/OD 415 nm ratios changing in accordance with winter versus summer conditions. These findings differ from those obtained by Carreras and Pignata (2001) in Argentina.

A comparison of the Ca content of *R. lacera* in the years 1978–2002 (Table 1) with the data of the Ca content of epiphytic lichens collected in unpolluted sites in the Mediterranean basin (Table 4), reveals that Ca accumulates in significant amounts, but is dependent on lichen species and site of collection. The Ca level in *Pseudevernia furfuracea*, for example, differs by one order of magnitude between central Italy and the north-eastern part of the country. The examples presented in Table 4, however, are not sufficient to consider these differences as a rule. The capacity of *P. furfuracea* to accumulate remarkable amounts of Ca is exemplified by samples collected in Turkey (Table 4), which are rather similar to those detected in *Ramalina maciformis* in the Negev Desert, Israel (Table 3).

The consistent accumulation of Ca in *R. lacera* in the years 1978–2002 probably involves the capability

Table 4
Selected Ca and K values detected in epiphytic lichens collected in unpolluted sites in several countries in the Mediterranean Basin. Means and SDs, on dry weight basis

| Lichen species | Location and country | Ca $\mu\text{g g}^{-1}$ | K $\mu\text{g g}^{-1}$ | Reference |
|--------------------------------|--|-------------------------|------------------------|--------------------------|
| <i>Hypogymnia physodes</i> | Control site, Northern Italy | 6163 \pm 1528 | 5301 \pm 1602 | Bergamaschi et al., 2007 |
| <i>Parmelia sulcata</i> | Control site, Northern Italy | 6014 \pm 898 | 6591 \pm 1814 | Bergamaschi et al., 2007 |
| <i>Pseudevernia furfuracea</i> | Control site, Northern Italy | 3041 \pm 622 | 4826 \pm 1369 | Bergamaschi et al., 2007 |
| <i>Usnea gr. hirta</i> | Control site, Northern Italy | 3242 \pm 621 | 6016 \pm 1602 | Bergamaschi et al., 2007 |
| <i>Evernia prunastri</i> | Remote site, near Colle di Val d'Elsa, Central Italy | 1556 \pm 7 | 2422 \pm 43 | Loppi and Frati, 2006 |
| <i>Pseudevernia furfuracea</i> | Reference area, Friuli-Venezia Giulia Region, NE Italy, Basal portion of the thallus | 12277 \pm 1518 | 2232 \pm 191 | Adamo et al., 2008a |
| | Lobes of the thallus | 12778 \pm 932 | 2240 \pm 141 | |
| <i>Flavoparmelia caperata</i> | Montagnola Senese, out of Siena, Central Italy | 20600 \pm 10002 | 4900 \pm 1300 | Monaci et al., 1997 |
| <i>Flavoparmelia caperata</i> | Natural Park “Oazi Zegna” near Ponzzone, Northern Italy | – | 6835 \pm 2050 | Rizzio et al., 2001 |
| <i>Flavoparmelia caperata</i> | Rural zone, near Tomar, center of Portugal | 13100 | 6300 | Godinho et al., 2008 |
| <i>Cetraria pinastri</i> | Rural site, Erzurum district, Turkey | 41840 \pm 2090 | 47350 \pm 2370 | Aslan et al., 2004 |
| <i>Pseudevernia furfuracea</i> | Rural site, Erzurum district, Turkey | 50850 \pm 2540 | 41580 \pm 2080 | Aslan et al., 2004 |
| <i>Evernia prunastri</i> | Rural sites, Giresum, Turkey | 14100 \pm 710 | 30980 \pm 1550 | Aslan et al., 2006 |
| <i>Pseudevernia furfuracea</i> | Rural sites, Giresum, Turkey | 65630 \pm 3280 | 37070 \pm 1850 | Aslan et al., 2006 |
| <i>Usnea florida</i> | Rural sites, Giresum, Turkey | 23220 \pm 1160 | 52100 \pm 2610 | Aslan et al., 2006 |
| <i>Usnea longissima</i> | Rural site, Giresum, Turkey | 20950 \pm 1050 | 32890 \pm 1640 | Aslan et al., 2006 |

of this lichen to convert large amounts of airborne Ca to calcium oxalate (Garty et al., 2002b). On the other hand, the temporal fluctuations of K, Mg, and Na (Table 1) suggest a different pattern of incorporation in comparison with the pattern suggested for Ca. The insignificant change of K concentrations in the lichen in HaZorea over the years is explained by their physiologically controlled location inside thallial cells.

Sodium, detected in the lichen *Ramalina canariensis* on the southwestern coast of Portugal, was found to decrease with greater distance from the coast (Figueira et al., 1999a,b). Similarly, elevated levels of Na in lichens collected near the Pacific Ocean in California confirmed the impact of the marine aerosol on the elemental content of lichens (Bennett and Benson, 2005). Sodium was found to attain the highest values in *Xanthoria parietina* collected along the coastal parts in a study area in the Aegean region in Turkey. However, high Na concentrations were found also in other sites, probably due to the contribution of soil (Yenisoy-Karakaş and Tuncel, 2004). The notion that Na is associated also with soil was corroborated by observations of lichens in Apostle Island, Wisconsin (Bennett and Wetmore, 2003). As the HaZorea Forest, investigated in the present review, is located about 20 km east of the Mediterranean coast, and is surrounded by many hills, it is reasonable to assume that the main contribution of Na is made by local soil and airborne dust. A previous temporal study with *R. lacera* from HaZorea (Garty et al., 1993b) did not detect significant fluctuation of Na content between December 1989 and February, April, and June 1990.

Table 1 shows that K values detected in *R. lacera* in the years 1993–2002 were similar to K values obtained for *Evernia prunastri* in central Italy and for *Pseudevernia furfuracea* in NE Italy (Table 4). On the other

hand, *R. lacera* reached lower values than other lichens in Italy and Portugal and much lower values than all lichens investigated in Turkey (Table 4).

The levels of Mg in *R. lacera* (Table 1) resembled those of other lichens in Italy and Portugal (Table 5), whereas the levels of Na in *R. lacera* were in the same order of magnitude as in *Evernia prunastri* in central Italy and in *Flavoparmelia caperata* from Portugal, yet much higher than those of *Pseudevernia furfuracea* in northeast Italy and *Flavoparmelia caperata* in central Italy (Table 5).

The mechanism of P uptake in *R. lacera* needs further investigation. Different studies demonstrated the capacity of lichens to absorb PO_4^{3-} from solutions (e.g., Farrar, 1976; Hyvärinen and Crittenden, 1998), or from rainwater under natural conditions. In the study area, airborne P is assumed to derive also from aerosols settling in the wake of dust storms (Ganor et al., 1991; Foner and Ganor, 1992). The negative correlation of Ca and P in *R. lacera* collected in the years 1978–2002 in HaZorea necessitates an analysis of the apparent antagonistic relations between the increased alkalinity caused by elevated amounts of Ca and the availability of phosphate ions in the lichen. An additional assumption that needs further investigation ascribes the decreased concentrations of P in *R. lacera* in HaZorea to the increasing rate of lichen growth, produced lately by the enhanced presence of nitrogen compounds, supposed to lead to a greater rate of dilution of P (compare with Hyvärinen and Crittenden, 1998).

P-containing compounds may derive from anthropogenic sources such as industrial plants producing phosphate-containing fertilizers. A study describing the use of the lichen *Rhizoplaca melanophthalma* as a biomonitor of the emissions of phosphate refineries in a semi-arid environment near Pocatello, Idaho, USA (Dillman,

Table 5
Selected Mg and Na values detected in epiphytic lichens collected in unpolluted sites in Italy and Portugal. Means and SDs, on dry weight basis

| Lichen species | Location and country | Mg $\mu\text{g g}^{-1}$ | Na $\mu\text{g g}^{-1}$ | Reference |
|--------------------------------|---|-------------------------|-------------------------|-----------------------|
| <i>Evernia prunastri</i> | Remote site, near Colle di Val d'Elsa, Central Italy | 746 \pm 3 | 244 \pm 1.53 | Loppi and Frati, 2006 |
| <i>Pseudevernia furfuracea</i> | Reference area, Friuli-Venezia Giulia Region, NE Italy | | | Adamo et al., 2008a |
| | Basal portion of the thallus | 738 \pm 69 | 39.4 \pm 9.3 | |
| | Lobes of the thallus | 806 \pm 40 | 38.2 \pm 5.1 | |
| <i>Flavoparmelia caperata</i> | Montagnola Senese, out of Siena, Central Italy | 900 \pm 800 | 93.3 \pm 18.7 | Monaci et al., 1997 |
| <i>Flavoparmelia caperata</i> | Natural Park "Oazi Zegna" near Ponzzone, Northern Italy | 1617 \pm 589 | – | Rizzio et al., 2001 |
| <i>Flavoparmelia caperata</i> | Rural zone, near Tomar, Center of Portugal | 581 | 835 | Godinho et al., 2008 |

1996), found negatively correlated concentrations for P in the lichen and distance from the refineries.

A comparison of the elemental content of the lichen *R. lacera* from HaZorea with that of an epiphytic lichen (*Protousnea magellanica*) collected in a remote, pristine area in the Nahuel Huapi National Park in northwestern Patagonia, Argentina, revealed lower or much lower Ca, K, and Na amounts in the Patagonian lichen: 976 ± 183 , 1510 ± 120 , and $63 \pm 18 \mu\text{g g}^{-1}$, respectively (Bubach et al., 1998). However, the Patagonian lichen contained similar levels of Mg ($909 \pm 130 \mu\text{g g}^{-1}$).

CONCLUSIONS

The analyses of Ca, K, Mg, Na, and P concentrations detected in thalli of the epiphytic lichen *Ramalina lacera* collected in a forested rural site did not reveal a linkage between chlorophyll integrity and alternating amount of specific elements contained in the lichen. The gradual increase of the number of dust storms originating in the Sahara Desert and the coincidental increase of the Ca content of *R. lacera* indicate the inherent capability of lichens to respond to global warming and desertification. To clarify this issue it is suggested to perform additional retrospective studies in the Mediterranean basin and in other regions of the world.

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