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The enigmatic enrichment of potassium and magnesium in runoff and floodwater in the Negev: Do biocrusts hold the key?

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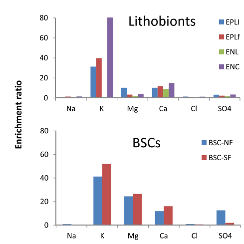
HIGHLIGHTS

- Runoff and floodwater in the Negev are enriched with variable ions.
- No satisfactory explanation was provided for K^+ and Mg^{2+} enrichment.
- Sprinkling experiments were conducted on rock- and soil-dwelling microorganisms.
- High enrichment ratios (up to 40-fold for K^+ and 10-fold for Mg^{2+}) were found.
- Suggestion: excretion following osmoregulation (K) and chlorophyll degradation (Mg).

GRAPHICAL ABSTRACT

The enigmatic enrichment ratio (ER) of K^+ and Mg^{2+} in floodwaters in the Negev

In comparison to no enrichment (ER=1), very high ERs were found for K^+ and Mg^{2+} by rock- and soil-inhabiting microorganisms in runoff, explaining the high concentration of these ions registered over the years in runoff water and floodwaters in the Negev



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ABSTRACT

Regardless of lithology and plant cover, chemical composition of floodwater in the Negev show a consistent enrichment in K^+ and Mg^{2+} ions, which could not have been explained by the rock or clay minerals or (due to the scarcity of plants) by plant decomposition. Hypothesizing that rock-dwelling (lithobionts) or soil (loess)-dwelling biocrusts may shed light on the phenomena, we conducted sprinkling experiments in the Negev Highlands. Sprinkling was conducted on 4 types of lithobionts: cyanobacteria which inhabit the south-facing bedrock (ENC), epilithic lichens, inhabiting the inclined (EPI_i) and the flat (EPI_f) north-facing bedrocks, and endolithic lichens (ENL) inhabiting south-facing boulders. Additional sprinkling took place on two types of soil biocrusts, a mixed crust composed of cyanobacteria, lichens and mosses at the north-facing footslope and a cyanobacterial crust at the more xeric south-facing footslope. The runoff water (of 5 and for 4 plots for each lithobiont and soil biocrust type, respectively) was analyzed for the ionic composition of Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, Cl^-, SO_4^{2-}, and NO_3^-, whereas HCO_3^- was calculated. In comparison to rainwater, all habitats (except for K^+ in ENL) showed high enrichment ratios (ERs) in K^+ and Mg^{2+}, which, unlike the high ERs of the other ions (such as SO_4^{2-} that may stem from gypsum dissolution), could not have been explained by the rock lithology, clay or dust composition. It is suggested that following wetting, K^+, serving for osmoregulation of cells, is released by the crust organisms,

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being thus responsible for K^+ enrichment, while chlorophyll degradation is responsible for Mg^{2+} enrichment. It is suggested that rock- and soil-dwelling microorganisms may explain K^+ and Mg^{2+} enrichment in runoff and floodwater and subsequently in groundwater of the Negev, and possibly in other arid zones worldwide, affecting in turn the quality of irrigation and drinking water.

1. Introduction

Whether in ground water (Sami, 1992; Panno et al., 1999; Marie and Vengosh, 2001; Edet and Worden, 2009), runoff and floodwater (Rampe et al., 1984; Edet and Worden, 2009), the composition of ions is of paramount importance. It may determine the water quality and subsequently its suitability for irrigation and drinking (Marie and Vengosh, 2001; Edet and Worden, 2009), and may play an important role in the structure and function of ecosystems.

This is especially the case for arid ecosystems. With water and nutrients being regarded as limiting factors for vegetation growth, runoff may not solely provide additional water but also essential nutrients to plants (Noy-Meir, 1973; Schlesinger et al., 1990). Redistribution of water and nutrients may therefore play an important role in shaping arid ecosystems, forming 'islands of fertility' for plants and animal activity within runon zones (Noy-Meir, 1973; Kidron and Aloni, 2018).

The ionic composition of runoff and floodwater was analyzed in many parts of the world (Rampe et al., 1984; Edet and Worden, 2009). Nevertheless, ionic composition of runoff or floodwater from arid areas is scarce (Ribolzi et al., 2003; Al-Qudah et al., 2015). Detailed examinations were however carried out in the Negev Desert, where a number of works attempted to study the relationships between the chemical composition of rain, runoff and floodwater (Nativ et al., 1983, 1997; Yair et al., 1991). All works found enrichment in the ionic composition of runoff and floodwater in comparison to rain (Yair et al., 1991; Nativ et al., 1997).

The enrichment was attributed to rock weathering, dust, surface salts and the diagenesis of clays (Nativ et al., 1997), and also to the burrowing activity of isopods and the presence of plants (Yair et al., 1991). Nevertheless, as admitted by Nativ et al. (1997), no satisfactory explanations were provided for the enrichment of some of the ions, such as potassium (K^+) and magnesium (Mg^{2+}), which showed exceptionally high enrichment factors (for instance: 10 and 3.8-fold higher for K^+ and Mg^{2+}, respectively; Nativ et al., 1997). Nativ et al. (1997) attributed the high amounts of Mg^{2+} in floodwaters to dolostone weathering, but high amounts of Mg^{2+} were also registered in limestone drainage basins (Yair et al., 1991; Kidron and Starinsky, 2020). As for K^+, while suggesting that it stems from pellets following isopod burrowing (Yair et al., 1991), Nativ et al. (1997) suggested that it may result from dust-laden clays (illite, feldspar). Nevertheless, since (a) the dust includes only small amounts of illite (Offer and Azmon, 1994), and (b) feldspar or illite diagenesis will require a parallel enrichment of Na^+ (while being in fact substantially lower), these explanations, as also admitted by Nativ et al. (1997), have serious flaws. In essence, no satisfactory explanation was provided for the high enrichment in K^+ and Mg^{2+}. Yet, all these works did not consider rock or soil-dwelling biocrusts as relevant candidates for the chemical enrichment of runoff and floodwater.

Biocrusts abound in the Negev Desert. They abound in the Negev Highlands (where they cover >90 % of the surfaces; Kidron and Temina, 2013), which generate most of the floodwaters in the Negev. They cover almost all the rocky surfaces, whether bedrocks, boulders or cobbles, and most of the soils and sediments, whether on sand (Kidron et al., 2000), or loess (Wilske et al., 2008). In the Negev Highlands, loessial soils abound, forming either aprons on the flat basins (Sede Zin) or accumulating as alluvium (along wadi beds) or colluvium (at footslopes) (Evenari et al., 1971). The rocks, principally calcareous, are covered by lithic biocrusts (lithobionts). This is especially the case for limestones that comprise the majority of the hills of the Negev Highlands.

Apart from sparsely distributed shrub-like fruticose lichens such as *Ramalina maciformis* (Lange, 1969), and some lichens that are loosely attached to the substrate (foliose lichens), most lichens are crustose and as such are tightly attached to the rock surface. By far, most lichens are chlorolichens, i.e., having green algae as their photobionts. They may either grow endolithically, i.e., embedded within the upper several millimeters of the limestone rock minerals (endolithic lichens) or epilithically, residing on top of the rock surface (epilithic lichens). Additionally, some of the rock surfaces are also covered by cyanobacteria, which like the endolithic lichens are embedded within the upper millimeters of the rock surface (Danin and Garty, 1983; Kidron et al., 2014a). Both endolithic groups render the surface unique appearance. While cyanobacteria render the surface a ragged appearance of grooves, endolithic lichens render the surface a jig-saw appearance (Danin and Garty, 1983). As for the loessial soils (desert lithosol or loessial serozem) scattered in between the rock outcrops, they are covered by cyanobacterial soil biocrust, i.e., biological soil crust (BSC), being accompanied by lichens and mosses in the more mesic habitats of the shaded (mostly north-facing) aspects, especially adjacent to rock outcrops where they benefit from additional supply of water (runoff).

Being either embedded within the rock and soil minerals or residing on top of the surface, biochemical interactions are expected to take place. Weathering by the lithobionts (Adamo and Violante, 2000; Aghamiri and Schwartzman, 2002) and the soil biocrusts (Chen et al., 2000) was indeed reported. Weathering was reported to take place due to the formation of carbonic acid following respiration by cyanobacterial and lichens, by a more elaborated mechanism that involves active extrusion of calcium ions through an active cellular uptake and transport process (Garcia-Pichel, 2006), due to the mechanical action of the tightly attached lichens (Fry, 1924; Lee and Parsons, 1999), or the excretion of various acids by lichens, such as oxalic, citric, gluconic, lactic, as well as unique acids known as 'lichen acids' (Barker and Banfield, 1996; Adamo and Violante, 2000; Chen et al., 2000). These weathering products are likely to be reflected in the runoff water. This is facilitated by the low infiltration rates of the rock and loessial surfaces. With rock and loessial surfaces generating runoff already following 2–4 mm h^{-1} and 5–7 mm h^{-1}, respectively (Blackburn, 1975), we hypothesized that the weathering action of biocrusts will be reflected in the ionic composition of the runoff water. Additionally, we also hypothesized that similar to plants, which may excrete certain elements (Brimblecombe and Todd, 1977; Crowther, 1987), or may enrich the runoff water following their decomposition (Lombin and Fayemi, 1976; Vitousek, 1977; Gosz, 1980), biocrusts may also have a unique signature on the chemical composition of runoff.

Redistribution of nutrients was indeed monitored during one hydrological year (2006/07), during which high enrichment factors of Ca^{2+} and HCO_3^- (attesting to rock weathering), and especially of K^+ (mainly by the cyanobacteria) and Mg^{2+} (mainly by the epilithic lichens) were recorded in runoff plots established on lithobionts in a small drainage basin near Kibbutz Sede Boqer (Kidron and Starinsky, 2020). While the enrichment in Ca^{2+} and HCO_3^- was explained by limestone weathering, the enrichment in Mg^{2+} was explained by the decomposition of the chlorophyll apparatus (which has high amounts of Mg^{2+}; Beraldi- Campesi et al., 2009) of the cyanobacteria and algal component of the chlorolichens. The enrichment in K^+ was also explained by the contribution of the microbial population that for osmoregulation purposes use K^+ and organic molecules (compatible solutes). While lichens may principally (but not solely) use organic molecules (but also K^+) for the osmoregulation (turgor pressure) of the cells, cyanobacteria and bacteria may use K^+ (but also organic molecules) (Hastings and

Gutknecht, 1976; Luard, 1982; Meury et al., 1985). Serving to preserve the cell integrity, it is accumulated within the cell during dry conditions. Once rewetted, and in order to prevent water entry into the cell and subsequently its membrane rapture (Kieft et al., 1987), K^+ excretion must take place. K^+ enrichment within the runoff water was therefore attributed to K^+ excretion by the cells, especially by cyanobacterial cells (Kidron and Starinsky, 2020).

While K^+ is essential for plant yield and common values do not harm humans (Krauss, 1997), lack in Mg^{2+} in drinking water may pose a threat to those populations that consume desalinated water (Rosen et al., 2018). Subsequently, measures are adapted to actively add Mg^{2+} to desalinated water (Birnhack et al., 2014). On the other hand, high amounts of NO_3^- in drinking water may negatively affect human health (Terblanche, 1991). With groundwater serving as an important drinking source, knowledge regarding the possible sources that contribute these ions is of prime importance.

The study of Kidron and Starinsky (2020) was however limited to one hydrological year (2006/07), during which some of the environmental conditions could not have been controlled. Thus for instance, the surface was characterized by variable amounts of dust (as a result of the different deposition rates over the slopes; Kidron et al., 2014b), and may have been subjected to variable rain intensities (subsequently impacting raindrop erosivity) in accordance with plot aspect and location (Kidron et al., 2014b). Also, runoff which is collected during field measurements is more prone to contamination (such as by insects that may enter the runoff buckets). Additionally, the ionic concentration of nitrate and ammonium was not examined, nor the chemical composition of runoff generated over soil biocrusts, which together with the rocky slopes, contribute runoff and floodwater to plants and groundwater. Toward this end, and in order to bridge our gap of knowledge, sprinkling experiments were conducted. Our goals were to (a) study the ionic composition of rock and soil covered organisms/microorganisms in comparison to rainwater and (b) to suggest possible mechanisms that may explain the enrichment or depletion of the ions. For these purposes, the Negev Highlands, responsible for providing most floodwater in the Negev (Hillel and Tadmor, 1962) was chosen, and specifically a drainage basin, which is lushly covered with lithobionts and soil biocrusts. Additionally, this site was also extensively studied during the last 30 years for its organism populations and the abiotic conditions that prevail at the different habitats, believed to increase our understanding regarding the abiotic-biotic relationships.

2. Methodology

2.1. The research site

The research site lies in the heart of the Negev Highlands near Kibbutz Sede Boqer, approximately 500 m amsl (34°46′E, 30°56′N; Fig. 1a). Long-term rain precipitation is 95 mm, falling principally between November and April (Rosenan and Gilad, 1985). Dew is

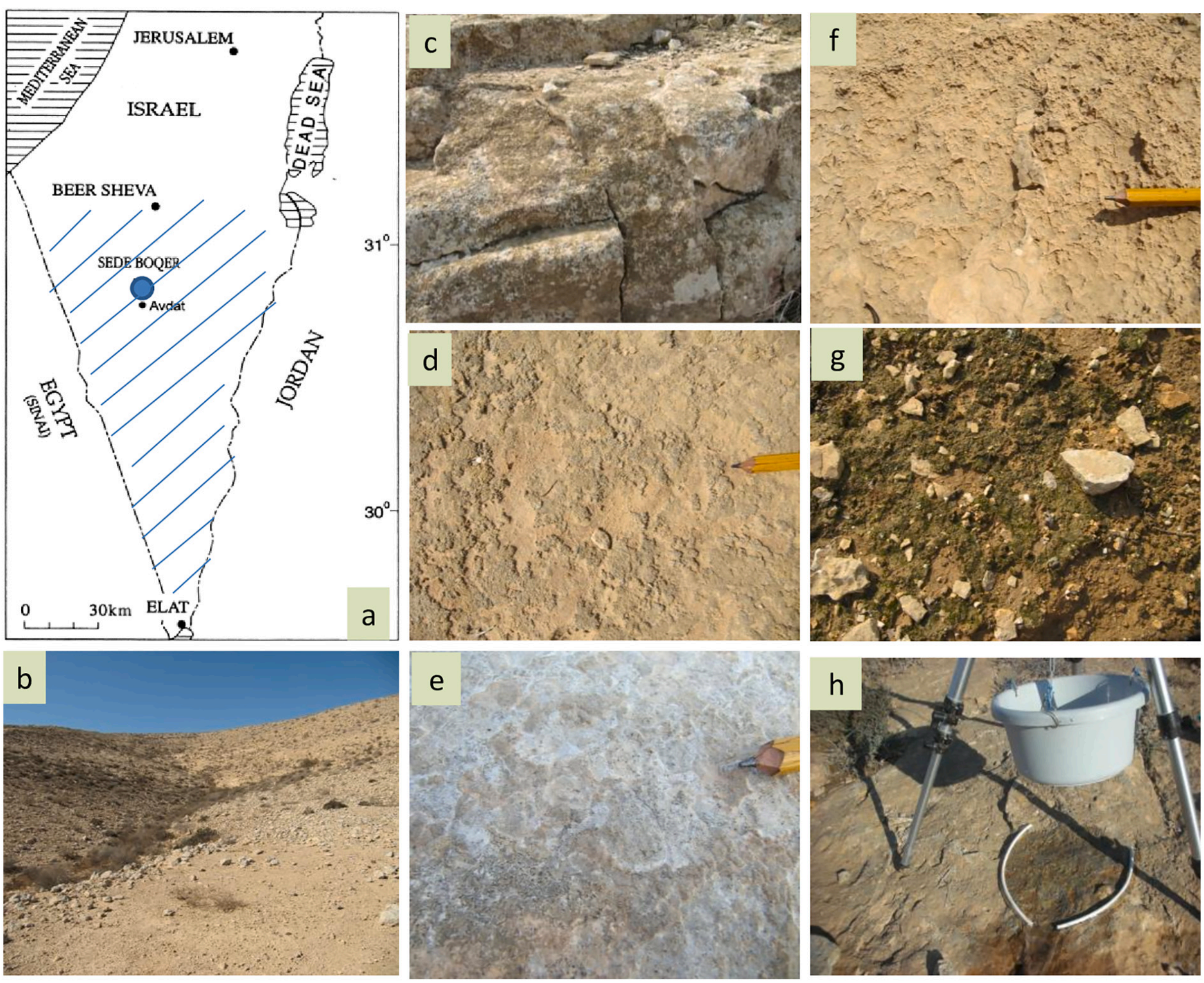

Fig. 1. Map of the Negev (indicated by slanted lines) (a) and general view of the research site (b), epilithic lichens covering inclined north-facing bedrocks (c), epilithic lichens covering relatively flat bedrocks (d), endolithic lichens covering a boulder at the south-facing slope (e), cyanobacteria covering south-facing bedrocks (f), soil biocrusts of mixed population of cyanobacteria, lichens and mosses at the north facing slope (g), and sprinkling on the lithobionts (h).

abundant, falling approximately for 200 days a year, with a mean annual dew amount of 33 mm (Evenari et al., 1971). Average annual temperature is 17.9 °C; it is 24.7 °C during the hottest month of July and 9.3 °C during the coldest month of January (Bitan and Rubin, 1991). Mean annual evaporation is ~2600 mm (Evenari, 1981).

The lithology is Turonian limestone (Arkin and Braun, 1965). Almost all rock surfaces and cobbles are covered by lithobionts, which show a distinct spatial distribution. Whereas endolithic cyanobacteria, ENC (with *Gloeocapsa* sp. predominating) cover the south-facing bedrocks, the south-facing rock particles (such as cobbles and boulders) are covered by endolithic lichens, ENL, with *Pyrenodesmia alociza (= Caloplaca alociza*) predominating. The north-facing bedrocks and rock particles are primarily covered by epilithic lichens (EPL) accompanied by ENL (mainly with *Pyrenodesmia alociza*) and cyanobacteria. While the epilithic lichens *Pyrenodesmia alociza* (= *Caloplaca aurantia*), *Aspicilia farinosa*, and *Lecanora albescens* predominate at the inclined north-facing bedrocks (EPL_i), *Caloplaca circumalbata* var. *bicolor* predominate at the flat bedrocks, EPL_f (Kidron and Temina, 2017). The flat bedrocks are characterized by a veneer of several millimeters of consolidated loess, presumably a result of long deposition and low erosion of the loess.

The spatial distribution of the lithobionts was explained by water availability. Unlike all lichen habitats, dew formation was not recorded at the south-facing bedrocks, and therefore did not benefit the ENC. Explained by the slow nocturnal cooling of the high-volume and sun-exposed south-facing bedrocks, which resulted in relatively high nocturnal temperatures, these bedrocks were found to benefit only from rainwater (Kidron et al., 2014a). On the other hand, the shaded north-facing bedrocks benefit from non-rainfall water (NRW), principally by dew and fog (Kidron and Kronenfeld, 2022a, 2022b). Experiencing efficient nocturnal cooling, and subsequently lower nocturnal temperatures (Kidron, 2000), high amounts of NRW also characterize cobbles, stones and boulders. The variable dew regime was found in turn to dictate species composition. While ENL predominate at the sun-exposed cobbles and boulders subjected to high but short-lasting dew amounts (Kidron, 2000), EPL predominate at the relatively shaded north-facing bedrocks and cobbles. As for the inclined north-facing bedrocks, while receiving only moderate amounts of dew, dew duration there lasts for long (Kidron et al., 2011, 2023).

Strips and patches (several meter wide) of loessial soil and large (up to dozens of meter wide) of colluvial-alluvial loessial soil cover the spaces in between the rocks at the slopes and at the footslopes, respectively. The soil is covered by soil biocrusts. While cyanobacterial biocrusts predominate at the south-facing slope (with *Microcoleus vaginatus* predominating), cyanobacteria (with *Microcoleus vaginatus* and *Nostoc* sp. predominating) accompanied by lichens (such as *Fulgensia fulgens* and *Diploschistes steppicus*) and mosses (*Tortula* sp.) characterize the north-facing slopes, with the lichens and mosses commonly inhabiting the more mesic habitats where water availability is higher, either due to runoff addition or due low evaporation (shading). Sporadic low-cover (<1 %) cyanolichens (lichens with cyanobacteria as photobionts) of the genus *Collema* sp. can be found on both slopes (but especially on the north-facing slope), being mainly confined to the rock-slope interfaces, where they benefit from additional water (runoff).

Extensive research aiming to study the water source of the soil biocrusts was also carried out. By attaching cloths to the soil surface, the amount of water obtained at 1 mm-thick air film (the cloth thickness) was possible. The findings showed that (a) nocturnal temperatures are too warm to facilitate condensation, excluding the possible formation of dew on the soil surface (Kidron and Kronenfeld, 2023), (b) wetting by rain and distillation provides the water required for biocrust growth (Kidron et al., 2022), and (c) addition of water, such as through runoff may result in high biomass biocrusts, commonly moss biocrusts (Kidron et al., 2010). These results show a clear disparity between habitats that also receive dew and fog and those solely benefiting from rain or rain-driven mechanism, i.e., distillation during which vapor from the wet ground may condense on the soil surface (Kidron et al., 2022).

2.2. Methods

The research was conducted on north- and south-facing slopes of a first-order drainage basin (Fig. 1b). Subjected to extensive research in the last 30 years, data regarding the microclimatological and ecological factors that affect the different habitats are available (Kidron et al., 2014a, 2023). Four types of rock (limestone) surfaces and two types of soil surfaces were chosen:

a. EPL inhabiting inclined north-facing bedrocks, EPL_i (Fig. 1c).
b. EPL dwelling on top of relatively flat rocks, EPL_f (Fig. 1d).
c. ENL which inhabit south-facing boulders, rendering a jig-saw appearance to the surface (Fig. 1e).
d. South-facing bedrocks inhabited by ENC, rendering a ragged appearance to the surface (Fig. 1f).
e. North-facing (BSC-NF) and south-facing (BSC-SF) soil biocrusts (Fig. 1g).

On each type of surface, 5 plots (approximately 30–40 cm diameter) for the lithobionts and 4 plots for the soil biocrusts were established. The lithobiont plots were demarcated with a 1 cm-diameter plastic-coated electrical wire that served as the plot boundary. The plots at the soil biocrusts were bounded by 10 cm × 0.5 mm thick metal sheets, inserted half way to the ground. During sprinkling, a gutter was used to drain the runoff water to plastic bottles at the bottom of each plot. In order to eliminate, as much as possible the effect of settling dust, the surface of the lithobiont plots were gently cleaned with a soft brush prior to sprinkling.

Sprinkling was conducted during April (lithobionts) and May (soil biocrusts), 2019. We used natural rain water that was collected during the preceding months. A 30 cm-diameter sprinkling device was used as previously described (Kidron and Büdel, 2014) at an intensity of 21 mm h^{-1} (Fig. 1h) The sprinkling lasted until 2 bottles, 250 ml each, were filled, approximately following 10 min and 20 min of sprinkling for the rocky and soil surfaces, respectively. The samples were immediately placed in a cooler and taken to a nearby lab, where they were immediately filtered using Whatman #42 filter papers. The filtered samples were measured for their pH and electrical conductivity (EC) using respectively Cyberscan PH11 and Cyberscan con11 (EuTech Instruments, Pte LTD, Singapore), and stored at 4 °C until processing.

All nutrients were analyzed according to standard procedures (Sparks et al., 2006). Calcium (Ca^{2+}) and magnesium (Mg^{2+}) were measured with SA 3000/5000 Skalar Segmented Flow Analyzer (Breda, The Netherlands); sodium (Na^{+}) and potassium (K^{+}) were determined by flame photometer; chloride (Cl^{-}) and sulfate (as sulfur, S) by Spectro CIROS CCD ICP optical emission spectrophotometer (Spectro Analytical Instruments, Kleve, Germany); NO_3^- was determined by ion analyzer while NH_4^+ was extracted with KCl solution. HCO_3^{2-} was calculated.

Additionally, the microrelief and the chlorophyll content of all surfaces were measured. The microrelief was determined at each plot with a microrelief meter having rods spaced at 3.1 mm apart, as described elsewhere (Kidron, 2007). The variance in rod height (in absolute values) represented roughness (Sanchez and Wood, 1987). Chlorophyll was determined by randomly taking 5 samples, 1 cm^2 each, from each plot. As for the endolithic cyanobacteria and lichens, they were immersed in water for 5 min to soften the substrate, and the top 10 mm of the rock was scraped using a sterile scalpel. The chlorophyll was extracted by hot methanol (70 °C, 20 min) in the presence of $MgCO_3$ (0.1 % *w/v*) in sealed test tubes and assayed according to Wetzel and Westlake (1969).

2.3. Statistical analysis

One-way ANOVA was performed in order to find possible differences between the biocrust biomass (chlorophyll), microrelief, pH, EC, and the chemical composition of runoff, with habitat serving as independent variable while chlorophyll content, microrelief, pH, EC, and the variable ions serving as dependent variables. The analysis was followed by Tukey's HSD post-hoc tests for each variable using IBM SPSS Statistics 22.0. Significant differences were regarded at $P < 0.05$.

3. Results

General properties of the lithobionts and the soil biocrusts are shown in Table 1. As far as the lithobionts are concerned, while epilithic lichens inhabit the north-facing and flat bedrocks and cyanobacteria inhabit the south-facing bedrocks, endolithic lichens inhabit the south-facing boulders. Noteworthy is the smooth surface of ENL. Also, although ENC and ENL face the south-facing aspect, they exhibited the highest and lowest relief, respectively. As for the soil biocrusts, both surfaces exhibited similar miocrorelief.

Expectedly, higher chlorophyll content characterized the shaded north-facing habitats, whether on the rock surfaces or soil. At the rock surfaces, the inclined epilithic lichens (EPL_i) had the highest chlorophyll content (103.2 mg m^{-2}), while the lithic endolithic cyanobacteria (ENC) had the lowest (18.9 mg m^{-2}). At the soil, north-facing biocrusts had on average more than twice as high chlorophyll content than south-facing biocrusts, 57.7 mg m^{-2} and 24.6 mg m^{-1}, respectively.

Expectedly, due to the limestone lithology, the predominate composition of the runoff water was $Ca(HCO_3)_2$. The ionic composition of the runoff water for the lithobionts and the soil biocrusts are shown in Tables 2 and 3, respectively.

The average amounts of ions for the lithobionts and for the soil biocrusts are shown in Figs. 2 and 3. The enrichment ratios (ERs) for the lithobionts and the soil biocrusts are shown in Fig. 4. As for the lithobionts, several points emerge:

a. All the lithic communities showed high ERs of Ca^{2+} (9.0–11.3) and especially of HCO_3^- (73.6–117.3), an expected outcome due to the limestone lithology. Halite dissolution resulted also in the enrichment in Na^+ and Cl^-.
b. Both types of epilithic lichens (EPL_i, EPL_f) showed very high ERs of K^+ (31.4–39.8) and high ERs of Mg^{2+} (3.4–10.3). They also showed high ERs for SO_4^{2-} (2.4–3.2).
c. In contrast to the epilithic lichens, no enrichment in K^+ was detected for ENL, but ENL showed high ERs for Mg^{2+} (2.1) and SO_4^{2-} (1.8).
d. ENC exhibited especially high ER of K^+ (80.4). They also exhibited high ERs of Mg^{2+} (4.0) and SO_4^{2-} (3.5). Nitrate and ammonium showed variable ERs. As for NH_4^+, while close to 1 in ENL (0.9) and slightly depleted in ENC (0.8), it was higher for EPL_i (1.7) and EPL_f (1.9). As for NO_3^-, while close to 1 in ENL (1.1), it was higher for all other lithobionts (1.4 for EPL_f and 1.8 for EPL_i and ENC).

To conclude, the chemical composition of all lithobionts showed, as expected, high ERs in Ca^{2+} and HCO_3^-. However, they also showed high ERs in K^+ (except for ENL), Mg^{2+} and SO_4^{2-}. Moderate ER was shown for NO_3^- for the epilithic lichens.

And as for the soil biocrusts:

a. High ERs of Ca^{2+} (11.9–16.1) and HCO_3^- (94.0–188.0) characterized both habitats, an expected outcome following the calcareous nature of the soils. On the other hand depletions in Na^+ and Cl^- were recorded.
b. Both biocrusts showed high ERs of K^+, (41.3–52.0), and Mg^{2+} (24.5–26.5), and fairly high ERs of SO_4^{2-} (2.0–2.6).
c. As for the NH_4^+ and NO_3^-, while BSC-NF showed almost no change in NH_4^+ (ER of 1.2), they showed a high ER (2.4) for BSC-SF. Substantially higher ERs were recorded for NO_3^- for both biocrust types (15.0–20.0).

Overall, and as indicated by the ANOVA results (Table 4), high variability in ion concentration characterized the different habitats, attesting to the habitat-specific traits and species compositions of each habitat. Of special interest was the enrichment of K^+ (except for ENL) and Mg^{2+} that could not have been explained by the lithology or dust. As for NO_3^- and NH_4^+, variable ERs characterized the different habitats.

4. Discussion

High variability in ion concentration characterized all lithic habitats. High variability also characterized all soil samples, even within the same aspect, explained by the high patchiness and clustered nature of many of these organisms.

All habitats exhibited high ERs for Ca^{2+} and HCO_3^-, an expected outcome given the limestone lithology of the site and the subsequent calcareous nature of the soils (Fernández-Ugalde et al., 2014). Dissolution of halite (which commonly accumulate at the surface following dust deposition and rainwater evaporation; Amit et al., 1993) may explain the enrichment of Na^+ and Cl^- in the lithic habitats. This however was not the case at the soil habitats, where a depletion of both ions (especially for BSC-SF) was recorded. The depletion of Na^+ can be explained by Na^+ exchange with Ca^{2+}-bearing calcite or illite (Sami, 1992), similarly to the exchange that takes place once sea water comes in contact with calcareous rocks (Carol et al., 2012; Ghiglieri et al., 2012).

All habitats showed high ERs for Mg^{2+} and except for ENL all habitats showed high ERs for K^+. All habitats also showed high ERs for SO_4^{2-}. As for SO_4^{2-}, high ERs for SO_4^{2-} were also reported in previous findings from the Negev (Nativ et al., 1983, 1997). It was explained by the composition of the rain (with SO_4^{2-} serving as condensation nuclei; see

Table 1
Properties of the lithobionts and soil biocrusts. Standard error in parenthesis. Cyano = cyanobacteria; endo = endolithic lichens; epi = epilithic lichens. Different letters indicate significant differences ($P < 0.05$).

Abbreviation	Type of lithobiont	Aspect	Angle (°)	Microrelief (mm cm^{-1})	Chlorophyll *a* (mg m^{-2})	Species composition (%)
EPL_i	Epilithic lichens (inclined)	North-facing	38	2.35 (0.30)	103.2 (9.0)	cyano (12) endo (25) epi (63)
EPL_f	Epilithic lichens (flat)	On relatively flat rocks	0–7	2.62[a] (0.25)	51.8[a] (14)	cyano (20) endo (20) epi (60)
ENL	Endolithic lichens	South-facing	12	0.84[b] (0.12)	53.3[a] (4.8)	endo (100)
ENC	Cyanobacteria	South-facing	28	2.91[a] (0.33)	18.9[b] (1.3)	cyano (100)
BSC-NF	Soil biocrusts (cyano, lichens, moss)	North-facing	15	2.58[a] (0.30)	57.7a (9.8)	cyano (40) lichens (20) moss (40)
BSC-SF	Soil biocrust (cyano)	South-facing	13	2.83 (0.35)	24.6 (1.6)	cyano (100)

Table 2
Ionic composition of the runoff water at the lithobiont habitats in comparison to the sprinkling water (rain). AVE = average; SD = one standard deviation (in italics). nd = no data.

Source	Na	K	Mg	Ca	NH_4	Cl	SO_4	NO_3	HCO_3	TDS mg/l	EC mS/cm	pH
Rain	0.110	0.0003	0.013	0.031	0.017	0.169	0.022	0.0032	0.003	11.1	0.02	6.09
EPLi	0.140	0.0003	0.058	0.330	0.017	0.226	0.059	0.0048	0.256	37.6	0.06	6.99
	0.140	0.0197	0.054	0.357	0.017	0.254	0.058	0.0065	0.268	40.7	0.06	7.04
	0.140	0.0003	0.042	0.305	0.051	0.254	0.065	0.0048	0.215	36.3	0.05	6.86
	0.110	0.0197	0.054	0.351	0.026	0.226	0.104	0.0065	0.223	38.5	0.06	6.99
	0.110	0.0003	0.103	0.254	0.034	0.282	0.071	0.0065	0.145	31.9	0.07	6.89
AVE	0.128	0.0080	0.062	0.319	0.029	0.248	0.071	0.0058	0.221	37.0	0.06	6.95
(SD)	*0.016*	*0.0110*	*0.023*	*0.042*	*0.014*	*0.024*	*0.019*	*0.0009*	*0.050*	*3.3*	*0.01*	*0.08*
EPLf	0.110	0.0197	0.040	0.322	0.042	0.226	0.050	0.0048	0.253	37.2	0.06	6.96
	0.110	0.0003	0.031	0.249	0.017	0.141	0.051	0.0032	0.212	28.8	0.05	6.95
	0.140	0.0304	0.052	0.552	0.042	0.226	0.057	0.0048	0.529	60.1	0.08	7.40
	0.330	0.0003	0.051	0.366	0.042	0.254	0.050	0.0048	0.480	57.3	0.06	7.14
	0.140	0.0003	0.046	0.339	0.017	0.197	0.054	0.0048	0.286	38.2	0.06	7.14
AVE	0.166	0.0102	0.044	0.365	0.032	0.209	0.053	0.0045	0.352	44.3	0.06	7.12
(SD)	*0.093*	*0.0140*	*0.008*	*0.113*	*0.014*	*0.043*	*0.003*	*0.007*	*0.143*	*13.7*	*0.01*	*0.18*
ENL	0.110	0.0003	0.024	0.252	0.008	0.141	0.037	0.0032	0.214	28.0	0.05	6.77
	0.110	0.0003	0.026	0.300	0.008	0.141	0.045	0.0032	0.255	31.9	0.05	6.95
	0.110	0.0003	0.026	0.244	0.026	0.169	0.033	0.0032	0.199	28.2	0.04	6.91
	0.110	0.0003	0.029	0.293	0.017	0.169	0.047	0.0048	0.228	31.6	0.05	6.94
	0.110	0.0003	0.029	0.316	0.017	0.169	0.036	0.0032	0.263	31.5	0.07	7.07
AVE	0.110	0.0003	0.027	0.281	0.015	0.158	0.040	0.0035	0.232	30.6	0.05	6.93
(SD)			*0.002*	*0.031*	*0.007*	*0.015*	*0.006*	*0.0007*	*0.027*	*2.0*	*0.01*	*0.11*
ENC	0.170	0.0003	0.076	0.435	0.017	0.339	0.129	0.0081	0.222	46.1	0.09	6.96
	0.210	0.0304	0.045	0.579	0.008	0.197	0.075	0.0048	0.596	65.6	0.08	7.17
	0.280	0.0003	0.043	0.325	0.008	0.226	0.049	0.0048	0.378	47.3	0.05	7.05
	0.110	0.0304	0.038	0.370	0.017	0.226	0.049	0.0048	0.286	40.0	0.06	7.04
	0.110	0.0414	0.055	0.628	0.017	0.169	0.075	0.0065	0.601	64.4	0.09	7.40
AVE	0.176	0.0206	0.051	0.468	0.013	0.231	0.075	0.0058	0.417	52.7	0.07	7.12
(SD)	*0.072*	*0.0190*	*0.015*	*0.131*	*0.005*	*0.064*	*0.033*	*0.0014*	*0.175*	*13.7*	*0.02*	*0.17*

Table 3
Ionic composition of the runoff water at the soil biocrusts in comparison to the sprinkling water (rain). AVE = average; SD = one standard deviation (in italics).

Source	Na	K	Mg	Ca	NH_4	Cl	SO_4	NO_3	HCO_3	TDS mg/l	EC mS/cm	pH
Rain	0.087	0.0010	0.002	0.030	0.008	0.113	0.013	0.0002	0.003	7.6	0.06	6.15
BSC-NF	0.048	0.0542	0.040	0.282	0.008	0.056	0.276	0.0016	0.099	30.8	0.11	6.83
	0.052	0.0588	0.059	0.368	0.008	0.113	0.130	0.0032	0.300	40.4	0.11	7.15
	0.077	0.0496	0.052	0.353	0.008	0.141	0.117	0.0032	0.279	39.3	0.11	6.77
	0.122	0.0483	0.075	0.423	0.016	0.141	0.104	0.0048	0.435	51.1	0.15	7.62
AVE	0.075	0.0527	0.057	0.356	0.010	0.113	0.157	0.0032	0.278	40.4	0.12	7.09
(SD)	*0.034*	*0.0048*	*0.015*	*0.058*	*0.004*	*0.040*	*0.080*	*0.0013*	*0.138*	*8.3*	*0.02*	*0.39*
BSC-SF	0.031	0.0801	0.057	0.441	0.024	0.056	0.027	0.0016	0.549	50.5	0.11	7.5
	0.028	0.0678	0.050	0.449	0.016	0.085	0.025	0.0032	0.499	47.9	0.09	7.35
	0.021	0.0609	0.072	0.524	0.024	0.113	0.016	0.0016	0.572	54.2	0.11	8.11
	0.039	0.0573	0.065	0.514	0.016	0.056	0.032	0.0032	0.600	54.7	0.10	7.74
AVE	0.030	0.0665	0.061	0.482	0.020	0.078	0.025	0.0024	0.552	51.8	0.10	7.68
(SD)	*0.007*	*0.0100*	*0.009*	*0.043*	*0.005*	*0.027*	*0.007*	*0.0009*	*0.042*	*3.2*	*0.01*	*0.33*

Nativ et al., 1985, and Levin et al., 1996) and by the SO_4^{2-}-rich dustfall, which was attributed to the contribution of gypsum assumed to originate from the sabkhas (playas) in North Sinai (carried by western winds) or the Golf Coast (carried by eastern winds) (Nativ et al., 1997). The dust may settle on the slopes, which upon wetting by rainwater may be partially dissolved, thus enriching the runoff water with SO_4^{2-}. Noteworthy however are the low enrichment ratios in ENL, which may be explained by the surface smoothness of ENL (Fig. 1e, Table 1), which hinders efficient dust entrapment.

As for the soils, with the north-facing slope exhibiting ~2–4-fold higher moisture content and ~ 2–3-fold higher organic carbon (OC) than the south-facing slope (Grishkan et al., 2021), and the fact that there is a close link between OC and SO_4^{2-} (Gobran and Clegg, 1992) and that organic acids act to impede crystallization of Ca^{2+} and SO_4^{2-} (Singh and Middendorf, 2007), crystallization of gypsum may be hindered in the north-facing slope, resulting in turn in higher availability of SO_4^{2-}, which may be therefore readily leached by runoff water.

Whereas the enrichment of SO_4^{2-} may be explained abiotically, i.e., by the presence of SO_4^{2-}-enriched dust, this is not the case for K^+ and Mg^{2+}. As for K^+, this enrichment could not have been explained by abiotic factors. Thus, release of K^+ from clay minerals, such as illite, should have been accompanied by a parallel release of Na^+ (Nativ et al., 1997). Also, located far from any source of pollution (such as source of SO_2^-, known to cause lichen mortality and subsequently K^+ release; Puckett et al., 1977), lichen degradation due to pollution could not have explained the high amounts of K^+ and Mg^{2+}. A biotic contribution remains therefore as the most plausible explanation.

Potassium is accumulated by all living cells, aimed to control the osmotic pressure and subsequently to achieve internal integrity and functionality. It is also used to activate many internal enzymes (Epstein, 1986). However, upon wetting by low-salinity water, K^+ excretion takes place to prevent water entry into the concentrated cell solution and the

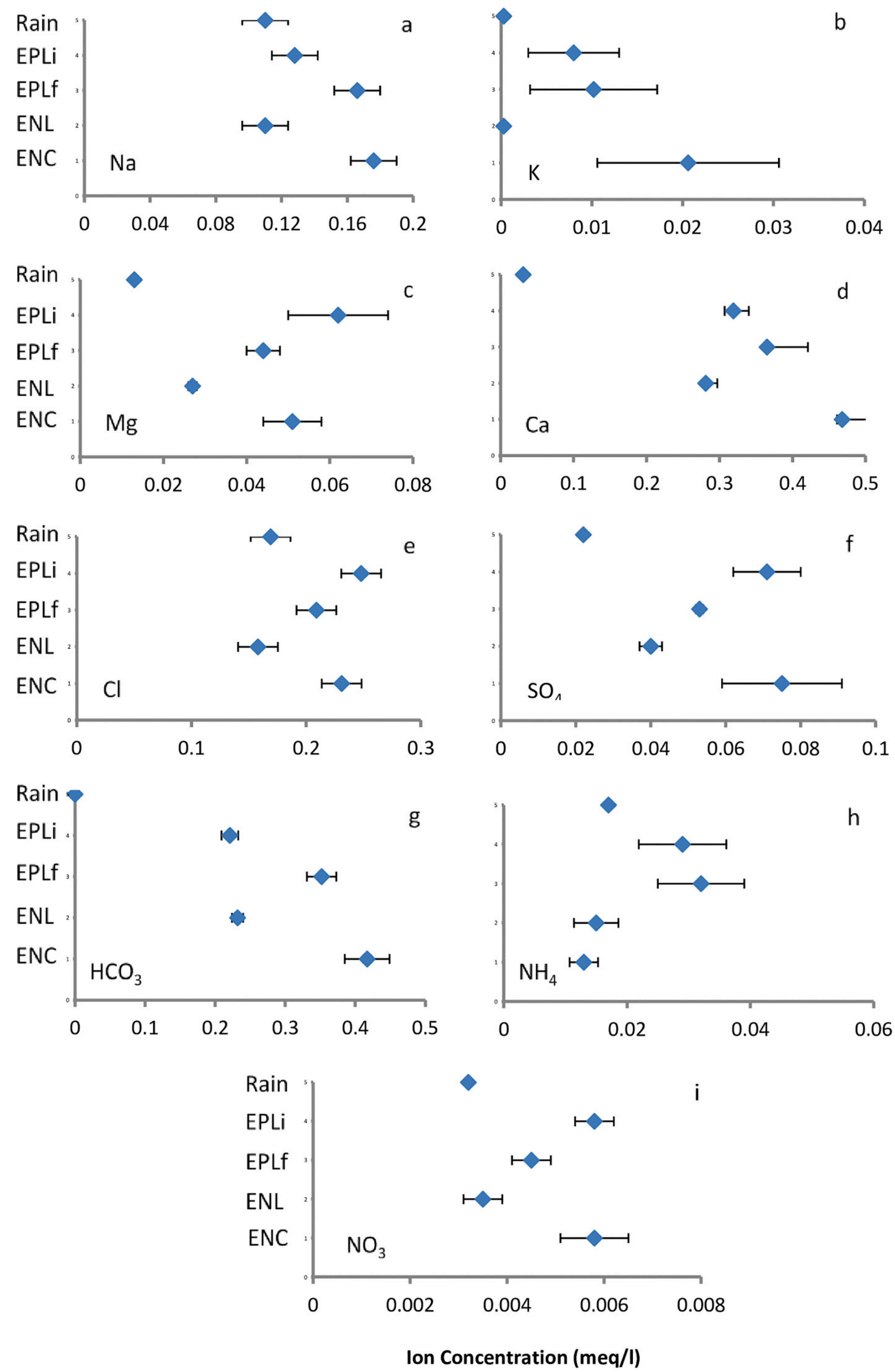

Fig. 2. Average ionic concentration (meq/l) of runoff generated from the different lithobionts in comparison to the sprinkled water. Note that the ionic concentration of HCO_3^- is calculated. Bars represent one standard deviation.

subsequent membrane rupture, which may be lethal for the cell (Kieft et al., 1987).

K^+ excretion was widely (but not solely) reported from prokaryotes, whether cyanobacteria, bacteria or archaea (Hastings and Gutknecht, 1976; Allison and Walsby, 1985; Meury et al., 1985; Reed et al., 1986; Galinski and Trüper, 1994). This may explain the K^+ enrichment at the south-facing rock-inhabiting cyanobacteria. Nevertheless, K^+ enrichment is not confined to cyanobacteria. Not only that K^+ is also used as osmoregulator by eukaryotes (Luard, 1982), and may therefore also be excreted by algae and fungi, but the excretion of K^+ can also be attributed to the presence of bacteria and cyanobacteria which accompany the lichens, similarly to the situation described in moss biocrusts, in which biocrusts that appear to be entirely covered by mosses, are also inhabited by cyanobacteria (Kidron et al., 2015).

As for Mg^{2+}, with rock composition having only negligible amounts of Mg^{2+} (as evident by environmental scanning electron microscope with energy-dispersive x-ray analysis of elements; Kidron et al., 2014a), only negligible amounts of Mg^{2+} are expected to stem from rock weathering. Moreover, if originating from the rock, a close link should have been noted between the amounts of Ca^{2+} and Mg^{2+}. This however was not the case (Fig. 2). Alternatively, with Mg^{2+} being an important structural element of the chlorophyll pigment (Beraldi- Campesi et al.,

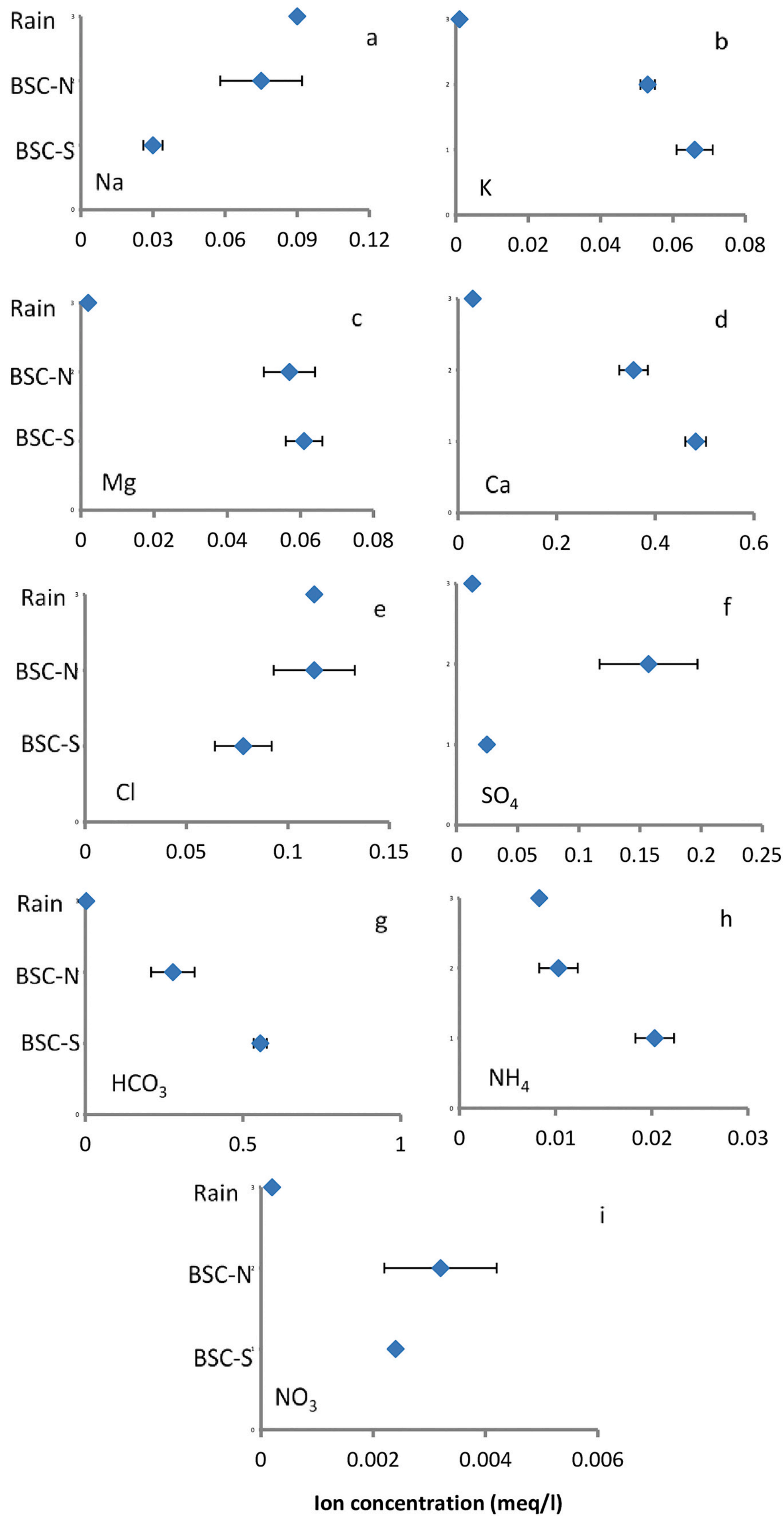

Fig. 3. Average ionic concentration (meq/l) of runoff generated from the north and south-facing soil biocrusts in comparison to the sprinkled water. Note that the ionic concentration of HCO_3^- is calculated. Bars represent one standard deviation.

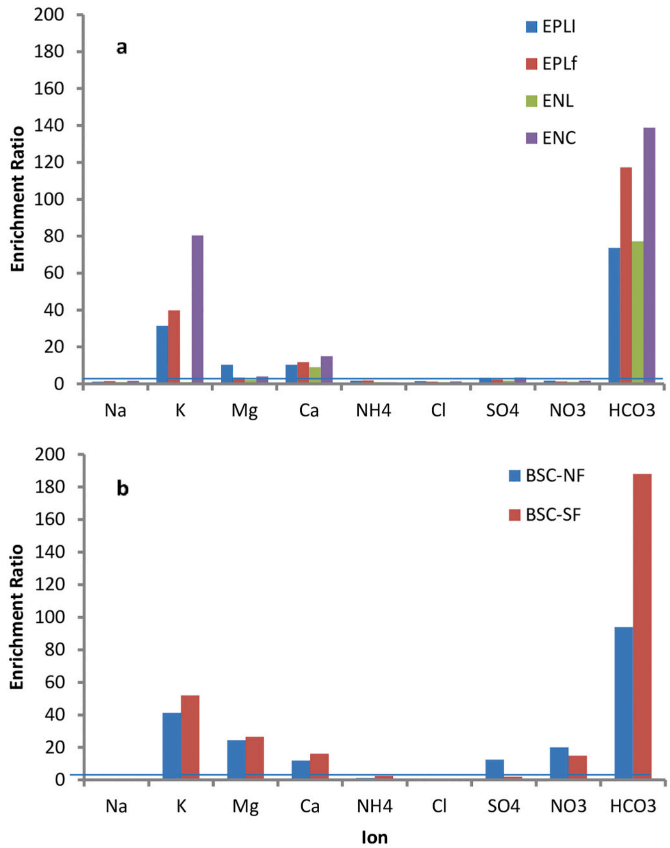

Fig. 4. The enrichment ratios of the different ions as calculated for the inclined epilithic lichens (EPL_i), flat epilithic lichens (EPL_f), endolithic cyanobacteria (ENC) and endolithic lichens (ENL) (a), and of the north-facing (BSC-NF) and south-facing (BSC-SF) soil biocrusts (b).

Table 4
Statistical analysis of pH, EC and each ion within the runoff water of lithobionts (a) and soil biocrusts (b). Significant differences are indicated in bold.

	(a) Lithobionts			(b) Soil biocrusts		
Variable	df	F	P	df	F	P
pH	3	2.726	0.085	1	5.192	0.063
EC	3	2.667	0.083	1	2.492	0.166
Na	3	1.381	0.285	1	6.680	**0.042**
Ca	3	3.976	**0.027**	1	12.060	**0.013**
Mg	3	5.219	**0.011**	1	0.266	0.063
K	3	2.072	0.144	1	6.159	**0.048**
NH_4	3	3.789	**0.032**	1	10.710	**0.017**
Cl	3	4.549	**0.017**	1	2.113	0.196
SO_4	3	3.809	**0.031**	1	10.720	**0.017**
NO_3	3	6.178	**0.005**	1	1.000	0.356
HCO_3	3	3.333	**0.046**	1	14.670	**0.009**
TDS	3	5.353	**0.010**	1	6.556	**0.043**

2009), we suggest that Mg^{2+} enrichment stems from the disintegration of the Mg-enriched chlorophyll apparatus, whether from the lichen photobionts (algae) or cyanobacteria.

Our findings provide also important insights regarding nitrogen availability. As for the lithobionts, whereas ERs of NH_4^+ showed a slight enrichment for EPL_f and EPL_i, it showed a slight depletion for ENC and ENL, which may point to the incapability of these communities to fix nitrogen and their dependency of allochtonous sources, i.e., rain, dew, and dust. Similar findings were also found for the cryptoendolithic community in the Dry Valleys of Antarctica (Friedmann and Kibler, 1980; Friedmann, 1982). As for NO_3^-, with the exclusion of ENL, all lithic habitats showed enrichment in NO_3^-, which support the occurrence of nitrifying bacteria, pointing also to adequate microaerobic conditions at these sites. Interestingly, although microaerobic conditions should also prevail in ENC, the lack of NO_3^- enrichment in this habitat attests to the absence of nitrifying bacteria. In this regard one should note that 10-fold higher amounts of NO_3^- than NH_4^+ characterize the Negev rains (Kidron and Starinsky, 2012), which may provide sufficient nitrogen to many lithobionts. Moreover, excluding ENC, all other lithic habitats benefit from dew, found to contain up to 3-fold higher amounts of NO_3^- in comparison to rain (Kidron and Starinsky, 2012). Apparently, NO_3^- may not be in shortage, especially in habitats that also benefit from dew.

As for the soils, NH_4^+ was mainly enriched in the south-facing slope. The relatively high proportion of cyanobacteria (in comparison to lichens) in the south-facing slope may explain the high enrichment of NH_4^+, similarly to the conditions recorded over cyanobacterial biocrust in the western Negev, which exhibited a relatively high gene (*nif*H) abundance responsible for N_2 fixation (Kidron et al., 2015). As for the NO_3^- enrichment, both slopes exhibit adequate conditions (occasional microaerobic conditions) to facilitate nitrification.

Our findings may have important implications. Previous analyses of rain and runoff water in the Negev showed high enrichment ratios in most ions. This include the enrichment of Na^+, Cl^-, and Ca^{2+}, attributed to rock weathering or dust input (Nativ et al., 1997), and the enrichment in SO_4^{2-}, attributed to the contribution of gypsum assumed to originate from sabkhas (Nativ et al., 1997). Nevertheless, as far as Ca is concerned, its enrichment may also be explained by biogenic weathering (Viles, 1995; Chen et al., 2000; Aghamiri and Schwartzman, 2002; Hoffland et al., 2004). On the other hand, some lithobionts, especially epilithic lichens, were also reported to provide protection against weathering (Mottershead and Lucas, 2000; Carter and Viles, 2005). Yet, the enrichment of Ca^{2+} also at the EPL habitats attests to rock weathering also at this habitats, and therefore, as far as our findings are concerned, the epilithic lichens do not exhibit pronounced bioprotection.

High enrichment in K^+ and Mg^{2+} were also recorded in humid regions, where it was principally attributed to plants, mostly plant residue, litter, or organic matter (Lombin and Fayemi, 1976; Herwitz, 1986; Marion et al., 2008), but also in drylands (Ribolzi et al., 2003; Al-Qudah et al., 2015), where the low cover of vegetation there does not support this explanation. In essence, no satisfactory explanation was provided for the high enrichment in K^+ and Mg^{2+} and as suggested above, the enrichment of K^+ and Mg^{2+} may stem from the lithobiont and biocrust contributions.

Of special interest is also the distribution of nitrogen, which was found to be enriched in the soils and groundwater of the Negev (Rosenthal et al., 1987). Similarly, high concentrations of nitrate were reported in soils and groundwater of many deserts, such as the Atacama (Ericksen, 1983), the Kalahari (Schwiede et al., 2005; Stadler et al., 2012), the Sahel (Edmunds and Gaye, 1997), the Mojave (Marrett et al., 1990; Al-Qudah et al., 2015) and arid Australia (Barnes et al., 1992). Commonly, and despite the low cover of plants, it was attributed to plant decomposition (Schade and Fisher, 1997), or to bacterial fixation which are associated with (yet scarce) leguminous plants (Edmunds and Gaye, 1997; Stadler et al., 2012). In the more mesic areas it was also attributed to bacteria associated with termite mounds (Barnes et al., 1992; Schwiede et al., 2005), to faecal pollution from cattle (Schwiede et al., 2005; Stadler et al., 2012), to fires (Barnes et al., 1992), aquatic cyanobacteria in occasionally inundated playas (Ericksen, 1983), or to a wetter paleo climate (Edmunds and Gaye, 1997; Marrett et al., 1990; Stadler et al., 2012). However, it was also attributed to fixation by soil biocrust (Mayland et al., 1966; Smith et al., 1990; Kidron et al., 2015). As found in our current findings, NO_3^- enrichment was recorded indeed in the soil biocrusts, but also in EPL_f, which may be linked to microbial activity within the consolidated veneer of loess that characterizes the EPL_f. Combined, these microorganisms may play an important role in explaining the high concentration of nitrate in the Negev soils and groundwater (Rosenthal et al., 1987).

The ionic enrichment in runoff is of utmost importance in regard to water redistribution, which is seen responsible for high vegetation cover at the rock-soil interfaces (Yair and Danin, 1980), or wadi beds, even supporting tall trees within hyper arid deserts (Evenari et al., 1961; Cohen et al., 1968; BenDavid-Novak and Schick, 1997). As previously reported (Kidron and Starinsky, 2020) and shown above, water redistribution may also result in nutrient redistribution, similar to the findings reported from humid karstic environments, where decomposition of lithobionts contributed nutrients to soil patches (Wang et al., 2016). Expectedly, the combined contribution of water and nutrients may explain the relatively lush cover of vascular plants at the feet of dunes (Kidron, 1999) and bedrocks (Yair and Danin, 1980) at the extreme arid ecosystems of the Negev.

Our findings may also have important application. Within moderate quantities, both K^+ and Mg^{2+} are essential components in drinking and irrigation water (Rylander, 2014). They are required by plants, animals and humans, and populations that consume desalinated water may suffer from shortage of Mg^{2+} (Rosen et al., 2018). On the other hand, high amounts of NO_3^- in drinking water may negatively affect human health (Terblanche, 1991). With groundwater serving as an important drinking source, knowledge regarding the possible sources that dictate the chemical composition of groundwater is of prime importance. Our findings may thus increase our understanding regarding the source and mechanisms acting to affect the chemical composition of groundwater.

5. Conclusions

Sprinkling experiments that were taking place over rock (lithic) and soil biocrusts in the Negev Highlands show variable enrichment ratios (ERs). High ERs for K^+, Ca^{2+}, HCO_3^- and Mg^{2+} were found for the epilithic lichens (whether on inclined, EPL_i or flat, EPL_f surfaces) and lithic cyanobacteria (ENC), but not for the endolithic lichens, ENL (except for HCO_3^- and Ca^{2+}). High ERs were recorded for K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, and NO_3^- for the soil biocrusts and the lithic biocrusts of both aspects, and also for SO_4^{2-} for BSC-NF. While abiotic factors may mainly explain the $Ca(HCO_3)_2$ composition of all habitats as a result of rock/calcite weathering and SO_4^{2-} enrichment may be explained by the contribution of rainfall and dustfall, biotic factors may explain the enrichment of Mg^{2+} (chlorophyll disintegration), K^+ (the excretion of K^+ ions from cells, principally prokaryotic due to osmoregulation) and NO_3^- (following ammonia nitrification). The results may explain high enrichments in K^+, Mg^{2+}, and NO_3^- in runoff, floodwaters and subsequently groundwater in the Negev, and possibly in other arid regions.

Authors' contribution statement

GJK and AS conceived and designed the research; GJK conducted the experiments; GJK, AS, and BX analyzed the data, wrote and edited the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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