Assessment of the cycle and availability of major and trace alkali and alkaline earth metals in the coastal Carmel Ridge, eastern Mediterranean

F. S. Kot¹ · M. Kochva¹

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Abstract

Major alkali and alkaline earth metals (Na, K, Mg, Ca) have been investigated extensively due to their role in soil, natural waters, living organisms, and agriculture, whilst their trace congeners (Li, Rb, Sr, Ba) are less well studied. Such information is of special interest for semi-arid Mediterranean ecosystems, in which these elements are believed to accumulate during prolonged dry seasons. However, data on the speciation, (bio)availability, and cycling of these metals are limited. We studied the fluxes of these metals in truly dissolved/reactive and ‘operationally dissolved’ (microfiltrate, $< 0.20 \mu\text{m}$) forms in the sequence of ‘rainwater–throughfall water–litter leachate’ in a restored mixed sclerophyll forest on the eastern Mediterranean coast. Truly dissolved metals were separated using an ion-exchange chromatography technique. The results suggest that decomposing plant litter followed by throughfall water are the main sources of the metals to underlying soils, whilst the contribution from rainwater is small, except for Na. Thereafter, the main flux of the water-mobile metals occurs within a semi-closed and rather self-sustaining soil–plant system. Only a portion of the water-mobile ($< 0.20 \mu\text{m}$) Na, K, Ca, and Mg was in truly dissolved/reactive form. The high-molecular-weight organic matter produced by leaf excretions in throughfall water and decomposing litter seems to play a major role in the speciation and transport of the metals, as well as in the mechanism of excretion of excess Na and Ca.

Keywords Flux · Precipitation · Throughfall water · Litter leachate · Truly dissolved · Ion-exchange chromatography

1 Introduction

In the biosphere, alkali and alkaline earth metals play an important role as they are essential elements in structural tissues and enzymes (Li, Na, K, Mg, and Ca). For Li, Rb, and Na, there has long been controversy regarding their value as nutrients for plants and animals [1–6]. Due to their chemical similarity, these metals often exhibit competing or synergetic effects in the biochemical and environmental processes; they are known to form coherent geochemical

couples, such as K and Rb, Mg and Ba, Ca and Sr [2, 7]. As part of biotic excretions and litter, these metals can be recycled through the complex processes of decomposition and synthesis, such as humification. In the terrestrial ecosystems, rainwater, when washing through and interacting with living plant foliage and then with plant litter, undergoes a series of physicochemical and chemical transformations before reaching the underlying soil. Dry atmospheric aerosols and dust also contribute to these processes [8–12].

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✉ F. S. Kot, fskot@technion.ac.il | ¹Department of Environmental, Water and Agricultural Engineering, Technion–Israel Institute of Technology, 3200003 Technion City, Haifa, Israel.

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However, there is limited information on the alkali and alkaline earth metals' turnover and availability in semi-arid ecosystems [13–18]. Li, Rb, Sr, and Ba are rarely considered in the professional publications or only the most general information is given (e.g. [1, 3, 19]). The information on the available forms of these metals is scarce, especially for the trace metals, except for the hazardous radioactive ^{137}Cs and ^{90}Sr isotopes which are products of many artificial nuclear technologies.

It is widely accepted that the mobility and availability of chemical compounds in the environment occur through association with water [2–4, 7, 20]. However, natural waters, including rainwater, throughfall water, plant litter percolate, and soil water, are highly heterogeneous systems, which contain metals in a wide variety of forms and compounds [7, 21–23].

Water-mobile metal compounds can roughly be divided into two major types [1, 24]: (1) reactive, which include truly dissolved compounds (hydrated ions and labile complexes) and easy-exchangeable compounds; both are considered as potentially (bio)available compounds; and (2) bound water-mobile compounds which are unreactive and (immediately) unavailable compounds such as mineral and organic complexes and colloids and living colloids (microbes).

Currently, the most common techniques that are used in environmental and geochemical studies to separate dissolved metals are microfiltration and centrifugation. In fact, such separation is only operational, and it does not carry any particular physical meaning [23, 25, 26]. The procedures remove suspended particles, coarse colloids, and most of the bacterial cells, except rod-shaped bacilli. Yet, fine colloids (organic, inorganic, and living) including viruses and fragments of bacterial cells, can infiltrate through the membrane filters. There are also more sophisticated techniques that are applied less often, such as ultrafiltration, reverse osmosis, liquid chromatography, stripping voltammetry, and diffusive gradients in thin films. However, they are laborious, and they have specific methodological disadvantages, such as the risk of sample contamination or the loss of the element from the sample [24, 27–30].

In the present work, we investigated the fluxes of both (1) truly dissolved/reactive and (2) bound water-mobile fractions of major and trace alkali and alkaline earth metals in a restored upland semi-arid Mediterranean forest in a coastal part of Carmel Ridge (northern Israel). The metals were determined in relation to the natural water flux sequence 'rainwater–throughfall water–plant litter leachate'.

In order to distinguish the truly dissolved/reactive form of the metals, a selective ion-exchange chromatography technique was applied [31]. The method has proven to be

effective for Li, Na, K, Rb, Mg, Ca, Sr, and Ba in the natural pH range. The method is simple in operation, and it is suited for sampling and preconcentration in fieldwork. The simplicity and the short list of reagents and laboratory ware used to have help with avoiding artificial contamination of the samples.

2 Materials and methods

2.1 Site description

The study area is a restored mixed upland forest, situated on the middle slopes of the north-western coastal part of the Carmel Ridge ($32^{\circ}46'42.6''$, $35^{\circ}01'31.8''$) (Fig. 1).

The area belongs to the semi-arid Mediterranean zone in the northern Israel. It is mountainous, and it is dominated by landscapes with steep slopes and relatively narrow valleys, with a low lying coastal plain. The climate is typically Mediterranean, with mild winters and warm and hot summers. The mean annual rainfall ranges between 600 and 900 mm. According to Yaalon [32], the excess of rainfall over evapotranspiration during winter months,

Fig. 1 Location of the sampling sites

varying from few mm to over 100 mm per month, is more important than the length of the dry season. The mean annual temperature is 19–21 °C; the mean temperature of the coldest month (January) is 10–13 °C and for the warmest month (July) it is 26–29 °C. The winds are mainly from south-west and bring dust material from the Sahara Desert.

The vegetation is a typical Mediterranean forest and maquis. Palestine oak (*Quercus calliprinos*) occurs in a more open and patchy mosaic of maquis and open shrubland. The open patches are dominated by either shrubs or herbaceous vegetation, which occur among the *Pinus* spp. trees. Carob tree (*Ceratonia siliqua*) is very commonly found in the western part of the ridge [33].

2.2 Sampling and analysis

Samples of rainwater and throughfall water were collected during the rainy season of the 2016/17 winter—from December 30 to March 25. Glass laboratory bottles equipped with plastic funnels with a diameter of about 25 cm were used for collecting rainwater in both open places and under the tree canopy (throughfall water) of species characteristic of the area, namely: Palestine oak (*Quercus calliprinos*), stone pine (*Pinus pinea*), and carob tree (*Ceratonia siliqua*). Each sampling variant was made in triplicate, and the mixed sample was prepared.

The samples were collected during every rainy event ($n = 21$) and filtrated through Whatman membrane filters of 0.20 µm. Truly dissolved/reactive compounds of the metals were separated using an iminodiacetate-grafted fibre (the IDA-fibre) [31]. The IDA functional groups are effective in the extraction of ionic and possibly other reactive compounds of alkali and alkaline earth metals [34].

In parallel, the concentrations of the metals were determined directly in the < 0.20-µm filtrates. The difference between the concentration of the metals in the filtrates and the concentration of truly dissolved/reactive metals was attributed to the content of bound water-mobile compounds.

Plant litter from under the trees were used in a pot experiment on litter leachate as described in Kot et al. [35]. Briefly, weighed amounts of the litter were put into plastic flowerpots, in accordance with the surface square from which they were collected. Rain events were imitated by spraying deionised water on the litter at a ratio of 1:1 of water compared to litter weight, to ensure that the litter remained wet and enable the decomposition process. In due time, the pots were sprayed with the usual portion of water, and 3 h later, an additional portion of water was sprayed on to enable the washing through of the decomposing material; the percolated leachates were collected in the under-pot saucer.

Selected physicochemical and chemical parameters of the water samples were measured, including pH, electroconductivity (EC), and light absorption at 254 nm. The last parameter was used to characterise the content of dissolved organic matter (DOM) in rainwater, which is, as a rule, below the sensitivity of the standard methods of C_{org} analyses. Weishaar et al. [36] showed that UV absorption at 254 nm, when normalised to dissolved organic carbon concentration, correlated strongly ($r^2 > 0.97$) with DOM aromaticity for a large number of humic substance isolates. Additionally, light absorption at 465 and 665 nm was measured to estimate the e4/e6 factor, which indicates the level of condensation of high-molecular-weight organic matter, including that of a humic nature that is typically part of natural waters. However, e4/e6 ratios have been shown to be better correlated with molecular size, O: C and C: N atom ratios, carboxyl content, and total acidity than to aromaticity [37–39] and, therefore, may be better suited as a general tracer of humification.

The input of Na, K, Rb, Mg, Ca, Sr, and Ba was evaluated based on: (1) the average data on rain in Israel [40] and (2) the obtained concentration of the metals in rainwater, throughfall water, and plant litter leachate.

Laboratory glassware and plasticware were pre-cleaned by filling them with 3% HNO_3 solution for 48 h and then rinsing them thoroughly with ultra-pure water.

2.3 Analytical determination of alkali and alkaline earth metals

The concentration of the metals was determined with the ICP-AES technique (Thermo Scientific iCAP 6300, England) calibrated with standard solutions from Inorganic Ventures, Inc. (Christiansburg, VA) and Merck KGA (Darmstadt, Germany). The detection limit of the method is 0.02 mg L^{-1} .

As the concentration of the metals was determined during extraction with the IDA-fibre, the detection limit for truly dissolved/reactive compounds was higher depending on the obtained volume of the sample—to 4 µg L^{-1} in the plant leachates, and from 0.8 to 0.03 µg L^{-1} in the rainwater and the throughfall water (see the corresponding tables in Results). Results on the verification of the technique can be found in Kot et al. [31].

For the major metals, the input both in truly dissolved/reactive and water-mobile forms was determined, whilst for the trace metals, only the input in the truly dissolved/reactive form was determined.

2.4 Key definitions

In the present work, the following definitions are used: (1) The concentration determined with ion-exchange

chromatography technique is referred to as the truly dissolved/reactive form of the metal, and (2) The bulk concentration determined in filtrate $< 0.20 \mu\text{m}$ is referred to as the operationally dissolved or water-mobile fraction of the metal.

3 Results

3.1 General physicochemical and chemical parameters

The physicochemical and chemical characteristics of the rainwater sampled in the coastal area of Carmel Ridge varied greatly (Table 1). It was predominantly sub-acid (pH 6.03); however, the pH values fluctuated over a wide range from 4.90 to 8.02. The sub-alkaline character of some of the rain events in the region is due to the action of carbonate/chalky dust brought from the southern deserts [41, 42]. The electroconductivity (EC) value was 0.036 mS cm^{-1} , whilst the concentration of water-mobile ($< 0.20 \mu\text{m}$) major metals (Na, K, Mg and Ca) was low. Content of DOM was small—according to values of light absorption at 254 nm .

The interaction of the rainwater with the tree canopy produced throughfall water with significantly different characteristics. Although the mean pH values increased only slightly, their amplitude narrowed significantly (Table 1), indicating the buffering capacity of the tree foliage. The EC values increased significantly, presumably due to the ions that were not determined in this work, such as NH_4^+ and organic compounds, since the concentration of the major metals only increased slightly. The concentration of DOM increased greatly.

In the litter leachate, there was a further decrease in the pH values and its amplitude. The sum of the major metals increased greatly, indicating that there was intensive litter decomposition during the rainy season. The concentration of DOM was significantly higher than that in the throughfall water.

The character of the DOM varied in the sequence of water fluxes: more condensed humic-like compounds prevailed in the throughfall water ($e_4/e_6 \leq 4$), whilst litter leachate produced fulvic-like compounds ($e_4/e_6 \sim 8$), which are less condensed and more mobile. Fulvic acids are known as effective binding and transporting agents for metals in the environment, including for alkali and alkaline earth metals [3, 43].

3.2 Alkali and alkaline earth metals

3.2.1 Rainwater

The concentrations of the major and trace alkali and alkaline earth metals in the rainwater are given in Tables 2 and 3. The contents of the major metals are in agreement with low rainwater mineralisation: the sum of water-mobile (operationally dissolved) Na, K, Mg, and Ca was 0.405 meq L^{-1} , but the value fluctuated over a wide range from 0.061 to 1.246 meq L^{-1} for individual rainfalls. These results correlate well with data on an operationally dissolved fraction ($< 0.45 \mu\text{m}$) of rainwater collected in the neighbouring basin of the Lake Kinneret (The Sea of Galilee) [44], except for Na. The concentration of Na was significantly higher in the coastal area of Carmel Ridge.

However, on average, only 23.5% of the sum of the major alkali and alkaline earth metals in the filtrates was determined in truly dissolved form, it only produced 0.117 meq L^{-1} . Moreover, the ratio between the water-mobile (operationally dissolved) and truly dissolved/reactive fractions of the metals differed greatly. In the water-mobile fraction, Na was a dominant metal comprising more than half of the sum of the metals, followed by Ca and Mg, whilst the portion of K was small:

$$\text{Na}_{(52.1)} > \text{Ca}_{(28.4)} > \text{Mg}_{(17.5)} \gg \text{K}_{(1.98)}.$$

However, when considering the truly dissolved/reactive fraction, Ca and Mg were the main metals, followed by Na:

Table 1 Selected physicochemical and chemical parameters of the rainwater, throughfall water, and plant litter leachate, from the coastal area of Carmel Ridge; median (min–max)

Object	pH	EC ($\mu\text{S cm}^{-1}$)	λ 254 nm	e_4/e_6	Σ metals* (meq L^{-1})
Rainwater [$n = 21$]	6.03 (4.90–8.02)	36.0 (24.0–131)	0.02 (0.01–0.13)	n.d	0.41 (0.06–1.10)
Throughfall [$n = 21$]	6.35 (6.07–7.33)	169 (60.0–550)	0.31 (0.06–1.18)	2.6 (1.8–4.0)	1.90 (0.64–25.4)
Litter leachate [$n = 18$]	6.70 (5.89–7.08)	—**	2.59 (1.45–4.00)	8.3 (5.4–15.1)	3.00 (1.22–23.8)

In brackets [], the number of samples is given

n.d. Not determined

*Water-mobile/operationally dissolved fraction

**Fluctuation of the signal

Table 2 Concentration of truly dissolved and water-mobile (< 0.20 µm) Na, K, Mg, and Ca in the water fluxes in the coastal part of Carmel Ridge, northern Israel (mg L⁻¹), $\bar{x} \pm S_x$, median (min–max)

	Na		K		Mg		Ca	
	Tr. diss	< 0.20 µm	Tr. diss	< 0.20 µm	Tr. diss	< 0.20 µm	Tr. diss	< 0.20 µm
Rainwater [n = 21]	0.94 ± 0.50 0.96 (0.37–1.59)	4.68 ± 4.03 3.89 (0.84–18.0)	0.09 ± 0.11 0.065 (0.01–0.51)	0.36 ± 0.27 0.24 (0.09–1.03)	0.44 ± 0.49 0.34 (0.02–2.18)	0.62 ± 0.38 0.49 (0.13–1.54)	0.83 ± 0.71 0.86 (0.03–2.79)	1.95 ± 2.27 1.43 (0.22–9.98)
Throughfall [n = 21]	1.47 ± 1.42 1.11 (0.20–5.91)	10.7 ± 4.99 11.3 (2.10–22.3)	0.42 ± 0.49 0.165 (0.01–1.52)	8.44 ± 10.0 4.53 (1.41–43.1)	0.90 ± 1.06 0.23 (0.07–3.31)	19.9 ± 40.1 3.06 (0.16–165)	4.66 ± 6.06 .99 (0.07–18.2)	71.8 ± 109 18.3 (1.67–396)
Litter leachate [n = 15]	3.20 ± 1.80 3.89 (0.19–5.51)	8.69 ± 1.43 8.50 (6.23–11.3)	5.96 ± 4.82 6.30 (0.14–12.7)	15.1 ± 10.2 14.7 (2.06–31.7)	7.77 ± 7.76 2.89 (2.14–20.5)	11.2 ± 12.4 3.57 (2.77–35.7)	10.4 ± 4.96 12.6 (3.81–16.4)	12.0 ± 5.81 15.1 (4.07–17.8)

In brackets [], the number of samples is given

Table 3 Concentration of truly dissolved/reactive Li, Rb, Sr, and Ba in the water fluxes in the coastal part of Carmel Ridge, northern Israel (µg L⁻¹), $\bar{x} \pm S_x$, median (min–max)

	Li	Rb	Sr	Ba
Rainwater [n = 21]	< 0.5	9.52 ± 6.8 10.9 (0.47–85.2)	3.35 ± 3.18 3.38 (0.10–30.8)	2.20 ± 1.52 2.15 (0.08–5.37)
Throughfall [n = 21]	< 0.5	55.0 ± 72.2 57.1 (2.7–242)	13.3 ± 17.1 13.7 (0.6–54.5)	5.01 ± 7.04 5.04 (< 0.1–26.5)
Litter leachate [n = 15]	< 0.5	98.3 ± 48.2 118 (35.0–156)	31.6 ± 19.1 30.0 (6.0–57.0)	83.9 ± 119 39.0 (6.0–317)

In brackets [], the number of samples is given

$$\text{Ca}_{(37.9)} \sim \text{Mg}_{(36.2)} > \text{Na}_{(24.1)} \gg \text{K}_{(1.72)}$$

The reason for this shift is an unexpectedly low portion of truly dissolved/reactive Na in rainwater, especially considering the coastal location.

Of the major metals in rainwater, Mg was the most soluble, indeed 71.0% of the element was determined in the truly dissolved fraction, followed by K and Na (21.0% and 19.8%, respectively), whilst most Ca was determined in bound/non-reactive form of the 0.20-µm filtrate (94.1%).

The concentration of truly dissolved Li in rainwater (as well as in throughfall water and litter leachates) was always below the sensitivity of the method, roughly < 0.5 µg L⁻¹, which is rather unexpected for an area with a semi-arid climate. In two large-volume samples of rainwater (> 1 L), the determined concentration of Li was even < 0.15 µg L⁻¹.

3.2.2 Throughfall water

Throughfall water is a product of rainwater washing through and interacting with the living plant canopy. In our case, the concentration of the water-mobile fraction (< 0.20 µm) of all the major metals increased significantly compared with rainwater (Table 2), by the following factors:

$$\text{K}_{(12.6)} > \text{Ca}_{(8.3)} > \text{Mg}_{(4.1)} > \text{Na}_{(1.9)}$$

This series is similar to that determined for Mediterranean sclerophyll oak-pine forests on calcareous rocks in the Montpellier region, southern France [13].

Most of the metals in the throughfall water were even more bound than in the rainwater: K (96.5%), Ca (94.8%), Mg (93.0%), and Na (91.0%), probably in the form of organic (humic-like) complexes of leaf excretions. (More detailed data for each tree species is given in Supplementary Table 1) The concentrations of bound Na, Mg and K, but not Ca, were positively correlated with the content of DOM: $r(21)$ for K was +0.57 ($p < 0.05$), for Mg it was +0.73 ($p < 0.01$) and for Na it was +0.78 ($p < 0.05$).

3.2.3 Plant litter leachate

The litter leachate that was obtained (Tables 2 and 3, Supplementary Table 2), when compared with throughfall water, contained more water-mobile K (factor of ~ 1.9) and about equal amounts of Mg and Ca, but much lower amounts of Na (factor of 0.3).

Compared with rainwater and throughfall water, the litter leachates contained a much higher portion of the truly dissolved/reactive metals (%):

$$\text{Ca}_{(45.4)} \sim \text{Mg}_{(44.7)} > \text{Na}_{(31.5)} \sim \text{K}_{(30.0)}.$$

It is interesting that among the major metals, only Na showed a significant correlation with the content of DOM. Moreover, the bound fraction of Na showed a positive correlation ($r(18) = +0.55$, $p < 0.01$), whilst truly dissolved Na, in contrast, correlated negatively ($r(18) = -0.44$, $p < 0.1$). Potassium showed the same trend, but with a lower statistical significance.

4 Discussion

4.1 Truly dissolved versus operationally dissolved fractions of the metals

One can see that the concentrations of the major alkali and alkaline earth metals obtained with the two techniques, i.e. (1) direct determination in filtrate ($< 0.20 \mu\text{m}$) and (2) ion-exchange chromatography, differ significantly. The concentration determined in the filtrate includes both the truly dissolved/reactive and bound water-mobile metal compounds, whilst the samples obtained with ion-exchange chromatography contained only the truly dissolved/reactive compounds, supposedly hydrated metal ions, labile compounds, and easily exchangeable metal compounds of the water-mobile colloids. Certainly, the bulk metal concentration in the filtrate will always be higher.

In this regard, a comparison of our data with data on precipitation in the neighbouring basin of Lake Kinneret (The Sea of Galilee) [44] situated roughly 60 km eastward is indicative. Foner et al. [44] reported the annual input of airborne elements in two forms, defined in the terms ‘dissolved’ ($< 0.45 \mu\text{m}$) and ‘solid insoluble’ ($> 0.45 \mu\text{m}$). One can see (Table 4) that the concentration of K, Mg, and Ca in water-mobile form obtained in the present work agrees well with the operationally ‘dissolved’ fraction obtained by Foner et al. [44], except for Na. The concentration of Na is higher in the coastal rainwater, due to the effect of the coastal marine aerosols. At the same time, the concentration of the metals in the truly dissolved/reactive form is significantly lower.

Based on these findings, some important methodological and practical questions arise. Firstly, the filtrates of natural waters can include both reactive and firmly bound metal compounds. As such, they can hardly serve as a measure of the reactive and (immediately) available compounds of the metals. The regular (micro)filtration/centrifugation technique can produce highly overestimated data compared with that from the more selective techniques such as ion-exchange chromatography. We suppose that the results obtained with ion-exchange chromatography technique are more definite and specific. They are closer to the concept of (truly) dissolved, reactive and bioavailable compounds.

Certainly, the process of the metals’ transformation and turnover in the environment is much more complicated. For example, some of the unavailable in the short period metal compounds can be effectively converted and utilised by biota through biochemical reactions [1–4]. Probably, a determination in parallel of both the truly dissolved/reactive and bound water-mobile forms of the metals (microfiltration) will promote a more precise and lucid understanding of the environmental processes.

4.2 On the alkali and alkaline earth metals cycle

The evaluated input of the metals in (1) truly dissolved/reactive form (Na, K, Rb, Mg, Ca, Sr, and Ba) and (2) water-mobile form ($< 0.20 \mu\text{m}$) (Na, K, Mg, and Ca) is given in Tables 5 and 6.

The input of water-mobile ($< 0.20 \mu\text{m}$) major alkali and alkaline earth metals with rainwater was characteristically low for the local precipitation (see also [41, 44, 45]). Sodium dominated among the metals. However, the bulk of the metals (including Na) were in bound and not (immediately) available forms, except for Mg ($\sim 29\%$). The ratio between the truly dissolved/reactive and bound forms varied greatly in all the types of water (Fig. 2).

For Na, the contribution of aerosol microparticles of continental/soil origin may be more significant (e.g. [12]) than the contribution from sea aerosols. For example, the presence of alkali feldspars and montmorillonite, for which Na is a characteristic element, has been determined in fine particles ($< 0.20 \mu\text{m}$) in winter atmospheric aerosols of the eastern Mediterranean [46, 47]. Mamane et al. [48]

Table 4 Input of water-mobile ($< 0.20 \mu\text{m}$) and truly dissolved alkali and alkaline earth metals with rainwater, throughfall water, and litter leachate, % of the total input, coastal area of Carmel Ridge

	Na		K		Mg		Ca	
	$< 0.20 \mu\text{m}$	Tr.d	$< 0.20 \mu\text{m}$	Tr.d	$< 0.20 \mu\text{m}$	Tr.d	$< 0.20 \mu\text{m}$	Tr.d
Rainwater [$n = 21$]	36.9	29.4	2.42	2.63	13.7	9.92	0.88	5.81
Throughfall [$n = 21$]	27.7	55.4	4.10	33.2	6.05	40.3	6.26	47.9
Litter leachate [$n = 15$]	35.4	15.1	93.5	64.2	80.2	49.8	92.9	46.3
Total ($\text{g m}^{-2} \text{year}^{-1}$)	2.60	13.2	2.69	9.11	2.48	4.94	10.2	24.6

Table 5 Input of truly dissolved and water-mobile ($<0.20\ \mu\text{m}$) Na, K, Mg, and Ca with rainwater, throughfall water, and plant leachate in the coastal area of Carmel Ridge, northern Israel ($\text{g m}^{-2}\text{ yr}^{-1}$), median (min–max)

	Na		K		Mg		Ca	
	Tr. diss	$<0.20\ \mu\text{m}$	Tr. diss	$<0.20\ \mu\text{m}$	Tr. diss	$<0.20\ \mu\text{m}$	Tr. diss	$<0.20\ \mu\text{m}$
Rainwater [$n=21$]	0.96 0.62 (0.37– 1.59)	3.89 2.54 (1.50– 6.44)	0.065 0.042 (0.01– 0.51)	0.24 0.21 (0.05– 1.88)	0.34 0.22 (0.02– 2.18)	0.49 0.36 (0.03– 3.19)	0.09 0.54 (0.03– 6.22)	1.43 0.94 (0.05– 10.4)
Throughfall [$n=21$]	0.80 0.72 (0.13– 3.84)	7.32 7.34 (1.32– 39.1)	0.12 0.11 (0.01– 0.99)	3.02 2.94 (0.27– 27.2)	0.16 0.15 (0.04– 2.15)	1.99 1.99 (0.53– 28.6)	0.64 0.63 (0.04– 11.8)	11.8 11.9 (0.74– 218)
Litter leachate [$n=15$]	0.92 2.53 (0.04– 3.57)	2.00 5.53 (0.09– 7.79)	2.51 4.10 (0.07– 8.25)	5.85 9.16 (0.16– 19.2)	1.99 1.88 (1.27– 13.3)	2.46 2.32 (1.57– 16.4)	9.49 8.19 (2.48– 42.5)	11.4 9.82 (2.97– 51.0)

In brackets [], the number of samples is given

Table 6 Input of truly dissolved Rb, Sr, and Ba with rainwater, throughfall water, and plant leachate in the coastal area of Carmel Ridge, northern Israel ($\text{g m}^{-2}\text{ year}^{-1}$), median (min–max)

	Rb	Sr	Ba
Rainwater [$n=21$]	0.009 0.006 (0.0005–0.085)	0.003 0.002 (0.0001–0.031)	0.002 0.001 (<0.0001 –0.005)
Throughfall [$n=21$]	0.011 0.011 (0.002–0.158)	0.002 0.002 (0.0004–0.035)	0.0008 0.001 (<0.0001 –0.017)
Litter leachate [$n=15$]	0.092 0.077 (0.023–0.430)	0.024 0.020 (0.004–0.138)	0.011 0.025 (0.004–0.207)

In brackets [], the number of samples is given

reported a significant variation in the Cl/Na ratio in aerosols on the eastern Mediterranean coast that were very different to the seawater values. However, most works on the chemistry and mineralogy of atmospheric aerosols in the Mediterranean basin and in Israel dealt with coarser particles ($>1\ \mu\text{m}$) from summer dust storms, whilst the fine solid aerosols of the winter rainy season can be quite different in origin and composition.

Additionally, the concentration of all major and trace metals in the truly dissolved/reactive fraction showed a significant correlation with the concentration of DOM: $r(21)$ were always $>+0.45$ ($p<0.05$).

A mechanism for the binding of Na and other metals during sea spray formation and transportation can be supposed. The high values of correlation coefficient indicate that the major complexing agent and carrier of the metals could be high-molecular-weight organic matter. In the throughfall water, this matter is the humic-like compounds of living foliage excretions. In the leachate of decomposing plant litter, it is the less condensed and more water-mobile fulvic-like compounds.

Low portion of Ca in the truly dissolved form (5.9%) is most likely due to the fact that its predominant form in local rainwater is calcite microparticles [41, 44]. Additionally, Foner and Ganor [49], investigating aerosols collected

in the city of Tel Aviv, has determined a surprisingly high, often dominant, content of gypsum.

For K, binding with feldspar and clay microparticles can be assumed.

The input of Rb, Sr, and Ba—in their truly dissolved/reactive form—was also low; the concentration of Li was always below the method's detection limit. However, there was no regional data available for Li, Rb and Ba for comparison. Regarding the few works that reported values on Sr, there are some doubts, since they do not have a proper description of the pure methods that are mandatory for working with trace elements.

The low Li migration ability and its low level of involvement in the local ecosystem were discussed in a previous paper [18]. Calcareous rocks, which dominate the area, are usually depleted in Li [50], but the soils developed over calcareous rocks probably are not [16, 51].

Rainfall was by far a secondary source of alkali and alkaline earth metals to the local soils—compared with waters enriched by their interaction with living plants and their litter (Table 7). However, for Na the contribution from rainwater was relatively significant. In comparison with the inputs obtained by Chapin [52] for evergreen and deciduous forests, the obtained percentages for Mg and Ca are similar and the percentage for K is two times lower.

Fig. 2 Input of truly dissolved/ reactive and bound water-mobile ($<0.20\ \mu\text{m}$) major alkali and alkaline earth metals in the water flux sequence, the coastal Carmel Ridge

The input of K, Mg, and Ca with solid aerosol particles [44] is also important, however, in bound forms. Whilst, for Na this source is of secondary importance (Table 7).

Since the input of water-mobile K, Mg, Ca, Rb, Sr, and Ba with rainwater is small compared with the input via throughfall and litter leachate, we can conclude that the main metal fluxes to underlying soils are the return

fluxes from vegetation. Therefore, we can talk about a semi-closed and rather self-sustaining cycle of these metals in the local soil–plant system. A similar phenomenon was previously found for boron [35]. Sodium is an exception, since the relative contribution from rainwater is significant for this element.

Table 7 Input of operationally dissolved and truly dissolved/reactive Na, K, Mg, and Ca with precipitation, northern Israel ($\text{g m}^{-2} \text{year}^{-1}$)

	Lake Kinneret basin [44]		Seaside Carmel Ridge (present work)	
	Solid particles*	Operationally dissolved ($< 0.45 \mu\text{m}$)	Water-mobile ($< 0.20 \mu\text{m}$)	Truly dissolved
Na	1.48–1.97	0.49–0.66	3.89	0.96
K	0.89–1.07	0.30–0.36	0.24	0.07
Mg	0.84–1.19	0.57–0.81	0.49	0.34
Ca	3.37–11.0	0.79–2.56	1.43	0.09

*Bulk (liquid and solid aerosol) precipitation minus operationally soluble fraction

Despite the rather brief contact between the rainwater and the living foliage, the resulting throughfall water is actually a separate kind of natural water due to its distinguishing physicochemical and chemical features.

The input of Ca via throughfall water was about equal to that from decomposing litter, indicating that leave excretion is an effective mechanism for removing an excess of Ca from plants. The local ecosystems are known for their saturation with Ca due to the prevalence of calcareous parent rocks and the effect of carbonate-bearing aerosols [32, 45, 48]. Unlike Na, K, and Mg, the bound fraction of Ca in the throughfall water and the litter leachate showed no positive correlation with the content of the DOM; prevalence of Ca in form of inorganic colloids can be supposed.

The largest Na flux was related with throughfall, it was two times larger than in rainwater and even larger than with litter leachate (3.7 times). Moreover, more than 90% of the element in the throughfall was in a bound form. Therefore, it can be assumed that any excess of this non-essential element is removed from plants by binding and excretion with high-molecular-weight organic matter.

In litter leachates, the metals were in fact more soluble and reactive compared with the throughfall water and even rainwater, with Mg being the most soluble. The reason is, probably, the less condensed character of the DOM of litter leachate and its lower binding capacity towards the metals, compared with the DOM of throughfall water. A contribution of soil microparticle/colloids for Ca in form of calcite microcrystals can also be considered.

Our observations on the character of DOM are in contrast to those for the humid subtropical forest of the southern Appalachian [10], where the effectively biodegradable DOM in the throughfall was determined and compared with that in the forest floor water (and soil water).

5 Conclusions

The results showed that the main input of K, Rb, Mg, Ca, Sr, and Ba to the local soils is the return flux from vegetation, in the form of decomposing litter leachate and throughfall water; Na is an exception, whereby the input due to rainwater and probably also to marine salt spray is significant. Rainwater was also a noticeable source of truly dissolved/reactive Mg, but a negligible source of truly dissolved/reactive Ca and K.

The input of K, Mg, and Ca with solid aerosols could also be important, but not for Na.

The filtrated samples of the waters included both reactive and firmly bound metal compounds. We suppose that the results obtained with ion-exchange chromatography technique are more definite and specific. They are closer to the concept of (truly) dissolved, reactive, and (bio)available compounds.

High values of correlation coefficient indicate that the major complexing agent and carrier of the metals in all the types of waters that were studied (including rainwater) could be high-molecular-weight DOM. In the throughfall water, this matter is the humic-like compounds of living foliage excretions. In the leachate of decomposing plant litter, it is the less condensed and more water-mobile fulvic-like compounds.

The concentrations of Li in the waters were always below the detection limit of the methods applied. This may be due to the low availability and involvement of Li in the ecosystems.

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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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