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RESEARCH PAPER

Base cation dynamics in rainfall, throughfall, litterflow and soil solution under Oriental beech (*Fagus orientalis* Lipsky) trees in northern Iran

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Abstract

· ***Key message*** **Fluxes of base cations were studied in an Oriental beech forest and an adjacent forest gap. The fluxes of base cations in throughfall, litterflow, topsoil and subsoil solution were higher in a mixed Oriental beech forest compared to the fluxes in rainfall and topsoil and subsoil solution in the forest gap. A large proportion of cations were adsorbed or biologically immobilised by passing through the litter layer in the forest. In the mineral topsoil, a new equilibrium between the solid phase and soil solution was established where desorption/leaching surpassed adsorption/immobilisation for Ca^{2+} and Mg^{2+} while the opposite was true for K^{+}. The contribution of throughfall is considerable in biogeochemical cycling.**

· ***Context*** Although it is important to measure nutrient fluxes to establish forest soil chemical fertility, little data is available for Oriental beech forests, one of the most important commercial hardwood forests in Iran. The quantification of nutrient fluxes above and below ground is essential because nutrients in the soil solution are most easily available for tree uptake. A thorough understanding of biogeochemical nutrient cycling requires an investigation of nutrient fluxes between different compartments.

· ***Aims*** We evaluated the effect of Oriental beech forests on biogeochemical cycling of Ca^{2+}, Mg^{2+}, K^{+} and Na^{+} by analysing their fluxes in rainfall, throughfall, litterflow and soil solution.

· ***Methods*** Throughfall, litterflow and soil solution were sampled during one whole year under five Oriental beech trees in a mixed Hyrcanian beech forest. The amounts of Ca^{2+}, Mg^{2+}, K^{+} and Na^{+} in these fluxes were calculated based on their concentrations and the sampled volumes and subsequently compared with the respective fluxes in the rainfall and soil solution of an adjacent forest gap.

· ***Results*** We found significantly higher fluxes in all the measured base cations in throughfall compared to rainfall. Entering the litter layer in the forest, nearly 50% of the dissolved base cations adsorb to the solid phase or are biologically immobilised prohibiting their leaching to deeper soil horizons. In the mineral soil, the interactions between the solid phase and soil solution were comparable between the forest and the forest gap.

· ***Conclusion*** This study highlights the role of interactions of rainwater with tree crowns and the litter layer in biogeochemical cycling and emphasises its importance for the maintenance of soil chemical fertility in Oriental beech forests.

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Contribution of the co-authors MM, HH, FK and AA developed the overall research idea, coordinated data collection and laboratory analyses. MM analysed the data with contributions from IB and SZ. MM, IB and SZ wrote the paper with contributions and input from all authors.

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1 Introduction

Base cations as part of the nutrient cycles in forests are tightly related to the hydrological cycle because water acts as the main solvent and transporting agent for nutrient elements between aboveground tree stands and the soil underneath (Bruijnzeel 2001). The composition of rainfall (RF) passing through a forest canopy and litter is generally altered because of interdependencies between dry deposition and rainfall, as well as ion-exchange processes depending on concentration gradients between canopy surfaces and rainwater (Schaefer et al. 1988). Furthermore, the strength of these processes depends on the biological activity of microorganisms, phenological phases, tissue exudation and decomposition (Návar et al. 2009). Soils in the environment support the growth of plants. The plants absorb the moisture and nutrients used for their growth and development from the soil. In the whole nutrient cycle, not only does the nutrient uptake play an important part, but also the leaching of nutrients from the plant biomass by precipitation and its return to the soil (Ward and Robinson 2000). Nutrients returned to the soil through stemflow, throughfall (TF) and litterfall help to maintain soil fertility by increasing the quantities of nutrients in the soil (Muoghalu and Oakhumen 2000).

Several studies have found that throughfall was enriched by base cations (especially K^+) compared to rainfall in all sorts of different forest types, which is related to foliage and canopy leaching or atmospheric deposition (Potter 1991; Staelens et al. 2003; Chuyong et al. 2004; Tobón et al. 2004a; Fujinuma et al. 2005; Dezzeo and Chacón 2006; Duchesne and Houle 2006; Adedeji and Gbadegesin 2012). Analogous investigations have been carried out in temperate forests which showed substantial leaching of the base cations potassium (K^+), calcium (Ca^{2+}) and magnesium (Mg^{2+}) from the canopy by throughfall compared to other cations (Potter 1991; Staelens et al. 2008; André et al. 2008; Van Stan et al. 2012). Leaching of base cations is affected, amongst other factors, by canopy structure, climate and the nutritional state of trees (Staelens et al. 2003).

Liu et al. (2002) found that base cation concentrations and fluxes were higher in throughfall relative to rainfall. They also reported that most K^+ and two-thirds of Mg^{2+} in throughfall was due to canopy leaching. Fujinuma et al. (2005) investigated species-related differences in nutrient cycling. They reported that K^+ had the greatest leaching in throughfall for all tree species while Ca^{2+} was the dominant cation in the forest floor leachate beneath basswood (*Tilia americana* L.) and hemlock (*Tsuga canadensis* L.), and K^+ and Ca^{2+} had equally high leaching for sugar maple (*Acer saccharum* Marsh.). Base cation release from litter leaching (litterflow, LF) is associated with degradation rate and quality of leaf litter, as demonstrated by numerous studies (Strobel et al. 2001; Van Nevel et al. 2013). Generally, concentrations of elements in both litterflow and throughfall follow the same pattern. Element outputs from litterflow were found to be strongly associated with the inputs from throughfall. In most cases, the average concentrations of nutrients such as K, Mg, P and the pH of litterflow were lower than those in throughfall (Tobón et al. 2004b). After the entry of litterflow into the mineral soil—a multicomponent system consisting of solid, liquid and gaseous phases—a new equilibrium state between these three phases is established. The cation exchange equilibrium is affected mostly by the distribution of cations between the solid and solution phase (Evangelou and Phillips 2005). The predominantly negative charge of soil colloids represents a huge reaction surface for cation adsorption which will potentially affect the chemical composition of litterflow entering the mineral soil.

Caspian forests, with an area of about 2,000,000 ha, are located between—20 and 2200 m a.s.l. in northern Iran. Pure and mixed beech stands are amongst the most important and richest stands of Hyrcanian forests. Beech forests cover about 17.4% of Iran's forests (Parsapajouh 1974), and Oriental beech (*Fagus orientalis* Lipsky) is one of the most important commercial hardwood species in Iranian forestry. Although many studies have been conducted throughout the world related to nutrient cycling by throughfall and stemflow, only a few studies have been done in relation to leached nutrients of litter and soil in forests dominated by Oriental beech. Abbasian et al. (2014) measured some nutrients in throughfall and gross rainfall in Oriental beech forests and found the average enrichment of K^+ in throughfall to be the highest. Salehi et al. (2016) concluded that concentrations of nutrients, and in particular K^+, in Oriental beech stands were generally higher in throughfall relative to rainfall. These investigations did not consider the chemistry of the soil solution and the role of the litter layer, however. Therefore, the present study compares the chemistry of the aboveground water fluxes passing through the tree canopy with the chemistry of the soil solution in a mixed stand of Oriental beech in Northern Iran as well as the analysed rainfall and soil solution of a nearby forest gap. It was expected that (1) throughfall in Oriental beech forests is significantly enriched with nutrient cations (K, Na, Mg, Ca) and that the annual input to the soil of these base cations by throughfall is significantly higher compared to the annual input by rainfall into the forest gap, (2) litterflow is depleted with base cations compared to throughfall due to exchange processes in the litter layer where adsorption and biological fixation predominates, (3) the fluxes of base cations in the mineral soil are significantly higher in the forest compared to the forest gap and (4) with increasing percolation depth in the mineral soil, the concentrations of base cations in the soil solution will further decrease due to the high adsorption capacity of the soil matrix.

2 Materials and methods

2.1 Site description

This study was conducted in a mixed natural Hyrcanian beech forest within district one (parcel 17 and 18) at the Shastkolate Forest Research Station of the University of Gorgan, located 5 km southwest of Gorgan, Golestan Province (36° 43′ N/54° 21′ E), northern Iran. District one covers approximately 1713.3 ha and its elevation ranges from 210 to 995 m a.s.l. The ground slope ranges from 0 to 80%. Mean annual precipitation is 649 mm ranging from 528 to 817 mm. The climate is moderately humid with an annual mean temperature of 15.4 °C. The area is dominated by natural temperate forests containing native mixed deciduous tree species such as Oriental beech (*Fagus orientalis* Lipsky), hornbeam (*Carpinus betulus* L.), Persian maple (*Acer velutinum* Boiss.), Persian ironwood (*Parrotia persica* (DC.) C.A.Mey.), Caucasian alder (*Alnus subcordata* C.A.Mey.) and black alder (*Alnus glutinosa* (L.) Gaertn.) (Moslehi 2010). The existing soil types are umbric fluvisols and chromic cambisols (IUSS Working Group WRB 2006).

A rectangular sample plot with an area of 0.5 ha and covered with a mixed stand of *Fagus orientalis* was selected at the border of parcel 17 and 18. The tree density in the sample plot was 96 trees ha^{-1}, with tree diameters varying from 7.5 to 105 cm and a canopy cover of 85%. The dominant tree species in the upper layer are Oriental beech (*Fagus orientalis* Lipsky) and hornbeam (*Carpinus betulus* L.). Additionally, Persian maple (*Acer velutinum* Boiss.) and Persian ironwood (*Parrotia persica* (DC.) C.A.Mey.) make up part of the forest stand. The understory vegetation is composed of *Rubus fruticosus* L., *Viola reichenbachiana* Boreau, *Ruscus hyrcanus* Woronow and *Pteridium aquilinum* (L.) Kuhn. The composition of the vegetation corresponds with the phytosociological unit of a *Fageto-Carpinetum*. The parent material is limestone, the soil texture is a silty clay loam and the elevation and slope of the sample plot are 550 m a.s.l. and 35% on average (highly variable), respectively (Moslehi 2010).

2.2 Field measurements

Five healthy and dominant beech trees with the same ecological conditions (topography, parent material, soil texture) were selected in the overstory of the sample plot. The selected trees did not overlap with adjacent trees (free canopy cover) in order to estimate the effect of canopy throughfall on base cation dynamics. The sample trees had a mean crown area of 221 m^2, a mean volume of 10.8 m^3, a mean basal area of 0.63 m^2, a mean diameter at breast height of 89 cm and a mean height of 34.6 m (Table 1). As a comparison reference to the forest stand, an open area in a forest gap with an area of 980 m^2 located 70 m away from the forest sample plot was chosen to measure rainfall as bulk precipitation.

Table 1 Allometric properties of Oriental beech trees in the mixed Hyrcanian beech stand

Tree no.	Crown area (m^2)	Volume (m^3)	Basal area (m^2)	D.B.H. (cm)	Height (m)
1	268	11.8	0.55	84	42.9
2	150	6.3	0.38	70	33.0
3	222	9.1	0.62	89	29.4
4	150	11.9	0.86	105	27.7
5	313	14.9	0.75	98	39.8
Mean	221	10.8	0.63	89	34.6

D.B.H, Diameter at breast height

Stemflow was not measured in the forest stand because it contributes only 0.3% to the total precipitation in beech forests in Shastkolate (Ghorbani and Rahmani 2009). The portion of incidental rainfall which passes through the canopy, either directly in gaps or after interacting with foliage and branches, is defined as throughfall (Parker 1983). The portion of throughfall which passes through the litter on the forest floor is defined as litterflow (Moslehi 2010). Rainfall (RF), throughfall (TF), litterflow (LF), topsoil and subsoil solution in the forest (TSF, SSF) and in the forest gap (TSO, SSO) were sampled monthly during an entire year from December 21, 2008 to December 21, 2009, comprising in total 32 rainfall events and one snowfall event (Fig. 1). For the sampling of throughfall, 20 cylindrical plastic collectors (23 cm in height, 7.75 cm in diameter) were randomly installed under each tree (fixed to a wooden peg 20 cm above the forest ground). In the forest gap, rainfall was collected with 20 galvanised rustproof containers (20 cm in diameter, 50 cm in height). A nylon mesh was placed at the opening of all collectors to prevent contamination by coarse debris. The collectors were emptied after each rainfall and rinsed with distilled water before being replaced.

Litterflow was sampled under each tree with ten randomly distributed cylindrical gauges (11.5 cm in height, 8 cm in diameter) under each tree, buried even with the ground and covered with a metal mesh. Freshly and previously fallen litter from beside the installed collectors was put on the metal mesh with a thickness of 2 to 5 cm (corresponding to the real thickness of the litter layer).

Under each of the sample trees in the forest, one soil profile was dug at a distance of at least 1 m from the trunk to a depth of 120 to 170 cm (Table 2). The physical characterisation of the profiles followed the Soil Survey Staff (2010) and Schoeneberger et al. (2012). In every soil profile, zero-tension lysimeters (galvanised rustproof containers, 5 × 5 cm) were installed in two depths, directly at the lower edge of the topsoil (0–10 cm) and in the subsoil (10–50 cm). An

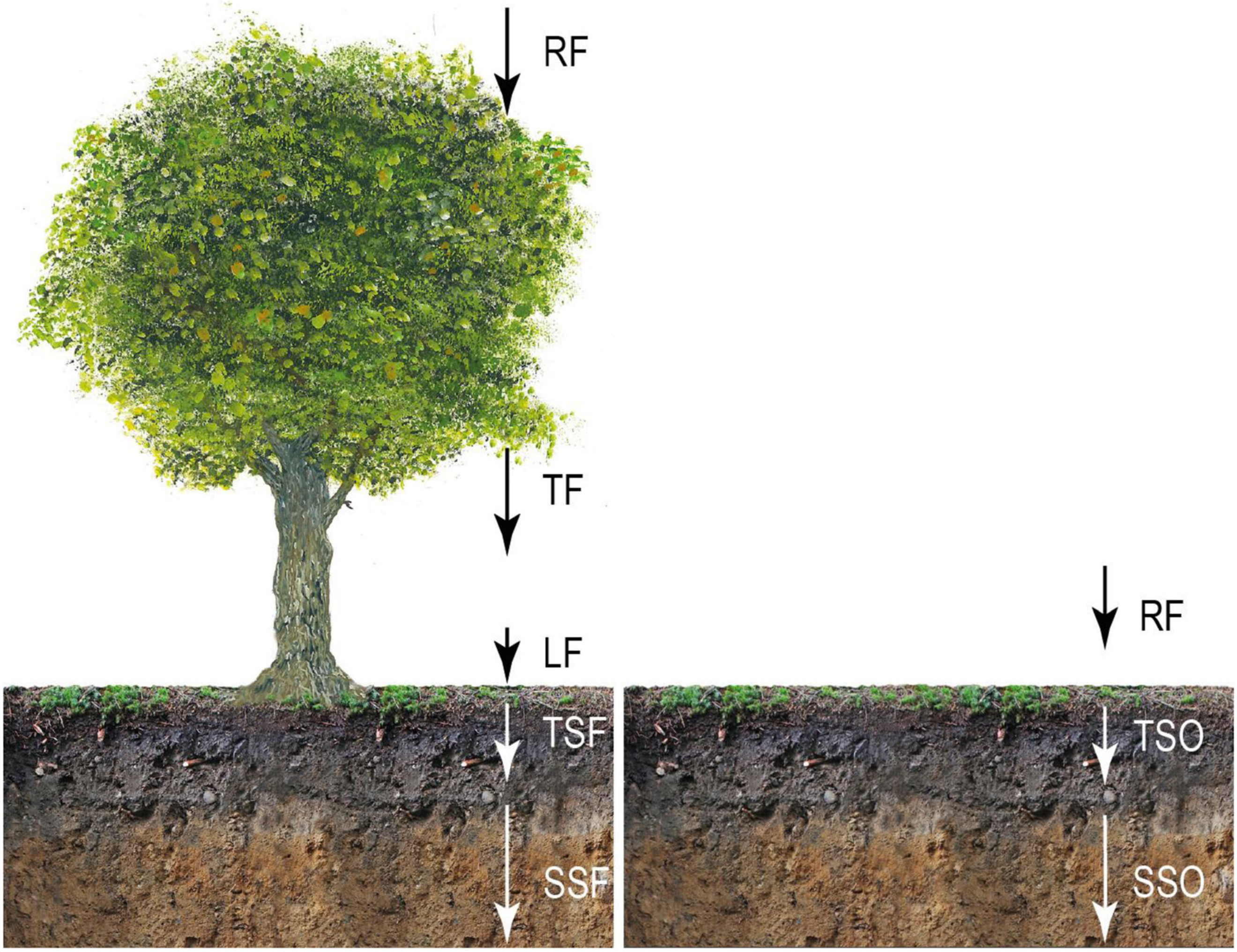

Fig. 1 Schematic representation of the fluxes in the forest (left) and the forest gap (right). RF, rainfall; TF, throughfall; LF, litterflow; TSF, topsoil leaching forest; SSF, subsoil leaching forest; TSO, topsoil leaching forest gap; SSO, subsoil leaching forest gap

additional soil profile was dug in the forest gap to a depth of 160 cm (Table 2). Here, five zero-tension lysimeters (galvanised rustproof containers, 5 × 5 cm) were installed independently of each other at the lower edge of the topsoil (0–10 cm) and the subsoil (10–50 cm). The lysimeters were connected to a 1-L plastic bottle via a discharge unit at the lowermost end and a flexible plastic tube (diameter 1 cm). Soil solution and litterflow were collected after each rain event.

2.3 Laboratory analysis

Physical and chemical soil properties in the forest and the forest gap were analysed from 12 samples of the topsoil and the subsoil. Soil samples were taken at the soil profiles at the depths of 0–10 cm and 10–50 cm and put into polyethylene bags for transportation to the laboratory. All samples were air-dried and sieved with a 1-mm mesh and analysed for pH, organic matter, $CaCO_3$ and soil texture. The analyses were made in triplicate. For each property, an internal reference soil was included in the analysis. Soil pH was measured potentiometrically (Smith and Doran 1996) in 0.01 M $CaCl_2$ (solid:solution = 1:2, under stirring after 30-min extraction time), $CaCO_3$ with calcimetry (Zarinkafsh 1992), organic matter using the Walkley–Black method (Nelson and Sommers 1996) and soil texture using the hydrometer method (Gee and Bauder 1986).

The volumes of soil solution collected were measured using a graduated cylinder, and the soil solutions were stored at 4 °C. The concentrations of base cations were measured on all water samples. Na^+ and K^+ concentrations were measured using flame photometry (PFP7 Jenway, Staffordshire, UK) (Smith and Doran 1996), and Ca^{2+} and Mg^{2+} concentrations were measured using atomic absorption spectrophotometry (UNICAM 919, Cambridge, UK) (Dewis and Freitas 1970). Standard solutions of titanium and lanthanum (LabKings, AA Grade 10 mg/l) served as internal standards. Annual amounts of the base cations in the various fluxes were calculated by multiplying the concentrations by the respective water volumes. The annual amount of soil solution was calculated based on the measured volumes of the soil solution.

2.4 Statistical analysis

The normality of variables and equality of variances was checked using the Kolmogorov–Smirnov and Levene's tests. Differences in the flux of the base cations between rainfall and throughfall, rainfall and litterflow, topsoil solution of forest and forest gap and subsoil solution of forest and forest gap were tested for significance using the *t* test. Significant statistical differences determined at the 95% confidence level were adjusted by applying the Bonferroni correction ($\alpha/4$ or 0.0125). The Bonferroni correction was used to reduce the risk of type 1 errors. All statistical analyses were performed with the software package SPSS 20 for Windows (IBM Corp. Released 2011. IBM SPSS Statistics for Windows, Version 20.0. Armonk, NY).

3 Results

3.1 Soil chemical and physical characteristics

In all soil profiles, the soil texture of the topsoil and subsoil was silty clay loam and clay, respectively, with no differences between the forest soil and the soil of the forest gap (Table 2). In the forest gap, higher pH values and $CaCO_3$ content in the soils were observed compared to the forest sites, which means that under the canopies of *Fagus orientalis* the pH values of the topsoil and the subsoil were about one pH unit lower than in the forest gap (Table 2). The mean organic matter content in the forest topsoil was, at about 7.0%, distinctly higher compared to the forest subsoil, at around 2.9%. In the forest gap,

Table 2 Physical and chemical properties of soil horizons in the forest and in the forest gap (according to the Soil Survey Staff 2010)

Soil profile	Horizon	Depth (cm)	Structure	Colour	pH ($CaCl_2$)	$CaCO_3$ (%)	OM (%)	Clay (%)	Sand (%)	Silt (%)	Texture
Tree 1	A	0–9	gr	10YR3/2	6.5	1.0	7.4	36	5.6	58	SiCL
	Bw1	9–50	2msbk	10YR4/3	7.2	26.0	3.1	61	2.9	36	C
	Bw2	50–80	2msbk	7.5YR3/3	–	–	–	–	–	–	–
	Bt	80–120	2cabk	7.5YR3/3	–	–	–	–	–	–	–
Tree 2	A	0–8	gr	10YR4/2	6.7	1.0	6.2	28	13.8	58	SiCL
	Bw	8–40	2fabk	7.5YR4/3	6.9	30.0	3.4	52	13.8	34	C
	Bt	40–89	2mabk	5YR3/3	–	–	–	–	–	–	–
	Bss	89–130	3cpr	7.5YR3/3	–	–	–	–	–	–	–
Tree 3	A	0–5	gr	10YR3/2	6.6	5.5	6.7	31	11.0	58	SiCL
	Bg1	5–38	1fabk	7.5YR4/4	6.5	13.0	2.2	59	2.8	38	C
	Bg1	38–70	2mabk	7.5YR3/3	–	–	–	–	–	–	–
	Bg2	70–100	2cabk	5YR3/3	–	–	–	–	–	–	–
	Bt	100–130	3cabk	5YR3/3	–	–	–	–	–	–	–
Tree 4	A	0–5	gr	10YR3/2	6.6	5.5	8.2	31	11.0	58	SiCL
	Bw	5–45	3msbk	7.5YR4/3	6.9	28.5	3.2	26	5.6	32	C
	Bt1	45–90	3csbk	2.5YR3/3	–	–	–	–	–	–	–
	Bt2	90–120	2mabk	5YR4/4	–	–	–	–	–	–	–
Tree 5	A	0–8.5	gr	10YR3/3	7.2	12.5	6.7	33	11.0	56	SiCL
	Bw	8.5–37	2msbk	10YR4/3	6.9	25.5	2.8	60	8.3	32	C
	Bt1	37–75	3cabk	7.5YR4/3	–	–	–	–	–	–	–
	Bt2	75–130	3cabk	7.5YR4/3	–	–	–	–	–	–	–
	Bk	130–170	2mabk	10YR4/4	–	–	–	–		–	–
Open area	A	0–10	gr	10YR3/2	7.7	23.0	2.0	30	16.5	54	SiCL
	Bw1	10–45	2mabk	7.5YR4/3	7.8	30.0	1.6	50	13.8	36	C
	Bw2	45–85	2mabk	7.5YR4/3	–	–	–	–	–	–	–
	Bw3	85–115	3mabk	2.5YR4/3	–	–	–	–	–	–	–
	Bw4	115–160	1cabk	5YR4/3	–	–	–	–		–	–

gr, granular; *abk*, angular blocky; *sbk*, sub-angular blocky; *pr*, prismatic; *f*, fine; m, medium; *c*, coarse; Si, silt; *C*, clay; *CL*, clay loam; *OM*, organic matter organic matter content was distinctly lower (topsoil 2.0%, subsoil 1.6%; Table 2).

3.2 Annual base cation inputs in rainfall, throughfall and litterflow

Single precipitation events in the forest gap (rainfall) ranged from 26 mm in spring to 127 mm in summer and accumulated to 970 mm for the whole observation period. The contribution of throughfall and litterflow to the total rainfall was 709 mm (73%) and 316 mm (33%), respectively (Table 3). Potassium was the dominant element in the base cation fluxes in rainfall, throughfall and litterflow, followed by Na^+, Ca^{2+} and Mg^{2+} (Table 3). The annual inputs of all these base cations in throughfall were significantly higher than in rainfall, with Δ TF-RF = 16.8 kg ha^{-1} $year^{-1}$ (64% of RF) for Na^+, 57.4 kg ha^{-1} $year^{-1}$ (105%) for K^+, 18.5 kg ha^{-1} $year^{-1}$ (196%) for Ca^{2+} and 2.9 kg ha^{-1} $year^{-1}$ (91%) for Mg^{2+} ($P < 0.05$; Table 3). The ratios of TF/RF were highest for Ca^{2+} (2.9), followed by K^+ (2.1) and Mg^{2+} (1.9) and lowest for Na^+ (1.6; Table 4). With the exception of Na^+, the annual fluxes in litterflow were also higher than in rainfall. However, the difference was only significant for Ca^{2+} (Table 3). The ratios of LF/TF in decreasing order were Mg^{2+} (0.7), K^+ (0.6) and Ca^{2+} and Na^+ (0.5). Thus, the element fluxes in throughfall were approximately twice as high as those in litterflow (Table 4).

Table 4 Ratios between fluxes of base cations in the forest and the forest gap

Site	Flux ratio	Na^+	K^+	Ca^{2+}	Mg^{2+}
Forest	TF/RF	1.6	2.1	2.9	1.9
	LF/TF	0.5	0.6	0.5	0.7
	TSF/LF	1.6	0.7	2.6	1.7
	SSF/TSF	1.0	0.6	1.0	0.9
Forest gap	TSO/RF	1.2	0.6	6.0	1.8
	SSO/TSO	0.6	0.5	0.6	0.5

RF, rainfall; *TF*, throughfall; *LF*, litterflow; *TSF*, topsoil leaching forest; *SSF*, subsoil leaching forest; *TSO*, topsoil leaching forest gap; *SSO*, subsoil leaching forest gap

3.3 Base cation leaching in soil solutions

The volume of water which percolated through the topsoil in the forest was 129% of the volume which passed through the litter layer, and in the subsoil, it was 82% of the volume which percolated through the topsoil (Table 3). Interestingly, more water percolated through the forest soil compared to the forest gap soil at both depths. In the forest gap, 34% of rainfall percolated through the topsoil and, of this amount, 73% percolated through the subsoil (Table 3).

With the exception of Ca^{2+}, the annual leaching of base cations from the forest topsoil was higher than the leaching in the forest gap, whereas the difference was only significant for K^+ (Table 3). The ratios of TSF/LF in the forest were highest for Ca^{2+} (2.6), moderate for Mg^{2+} (1.7) and Na^+ (1.6), and lowest for K^+ (0.7) (Table 4). In the subsoil, Na^+ and K^+ leaching was significantly higher in the forest compared to the forest gap, whereas there was no or only a small insignificant difference in the leached amounts for Ca^{2+} and Mg^{2+}. In the soil solutions of the subsoil of the forest, and in the topsoil and subsoil of the forest gap, the leached amounts

Table 3 Mean annual inputs of water and base cations (mean ± SE; $N = 5$) in the forest and the forest gap, with comparisons of fluxes between the forest and the forest gap

Site	Flux section	Water (mm $year^{-1}$)	Na^+	K^+ (kg ha^{-1} $year^{-1}$)	Ca^{2+}	Mg^{2+}
Forest	RF	970 ± 7.6	26.3 ± 0.5	54.6 ± 1.5	9.5 ± 0.4	3.2 ± 0.2
	TF	709 ± 26.5	43.1 ± 1.2	112.1 ± 6.9	28.1 ± 2.4	6.1 ± 0.7
	LF	316 ± 22.4	21.3 ± 1.6	65.8 ± 5.6	14.2 ± 1.1	4.5 ± 0.3
	TSF	408 ± 20.7	33.3 ± 1.9	49.1 ± 4.0	36.4 ± 2.3	7.7 ± 0.9
	SSF	336 ± 27.5	31.8 ± 2.9	31.8 ± 2.6	35.2 ± 6.3	6.6 ± 1.0
Flux differences		Δ TF-RF	16.8*	57.4*	18.6*	2.9*
		Δ LF-TF	− 21.8*	− 66.3*	− 13.9*	− 1.6*
		Δ LF-RF	− 5.0	11.2	4.7*	1.3
Forest gap	RF	970 ± 7.6	26.3 ± 0.5	54.6 ± 1.5	9.5 ± 0.4	3.2 ± 0.2
	TSO	327 ± 10.1	31.3 ± 0.9	30.4 ± 0.9	56.9 ± 1.6	5.7 ± 0.3
	SSO	239 ± 15.1	19.2 ± 0.8	15.5 ± 0.5	36.5 ± 2.8	2.8 ± 0.1
Flux differences		Δ TSF-TSO	2.0	18.7*	− 20.5	2.0
		Δ SSF-SSO	12.6*	16.3*	− 1.3	3.8

(*Significant at $P < 0.05$). *RF*, rainfall; *TF*, throughfall; *LF*, litterflow; *TSF*, topsoil leaching forest; *SSF*, subsoil leaching forest; *TSO*, topsoil leaching forest gap; *SSO*, subsoil leaching forest gap of base cations were in decreasing order: $Ca^{2+} > Na^{+} \approx K^{+} > Mg^{2+}$. Only in the topsoil of the forest, K^{+} was highest, followed by Ca^{2+}, Na^{+} and Mg^{2+} (Table 3). The ratios of SSF/TSF and SSO/TSO were all between 0.5 and 1.0, with the highest values for Ca^{2+} and Na^{+}, and the lowest values for Mg^{2+} and K^{+} (Table 4).

4 Discussion

4.1 Chemical and physical characteristics under beech trees and forest gap

Our results showed lower pH values in the uppermost 50 cm of the soil under Oriental beech trees compared to the open area in the forest gap. Possible sources of H^{+} ions include oxidation of biomass and NH_4^{+}, root respiration with the formation of carbonic acid, exudation of organic acids by the roots and/or organic acids produced by incomplete litter decomposition (Guckland 2009). Finzi et al. (1998) and Neirynck et al. (2000) reported lower pH values and base saturation under the canopies of *Fagus* species compared to *Tilia*, *Fraxinus* and *Acer* species. They attributed this finding to the interspecific differences of the acidification potential of the tree litter. The litter in the forest gap is mainly composed of herbs and grasses, whose palatability for the soil biota is much better compared to litter from beech. Therefore, the mineralisation of the litter in the forest gap is more complete, and fewer organic acids are produced leading to a higher pH value in the forest gap. This is analogous to what occurs in mixed stands, where the litter quality of different species and the associated base cation recycling through the soil-tree system have important effects on the pattern of soil fertility and soil acidity (Nordén 1994; Rothe and Binkley 2001). Therefore, litter composition can be assumed to be a significant factor in surface soil acidity (Guckland 2009). In accordance with the lower pH values in the forest, the $CaCO_3$ content in the forest topsoil is lower in comparison to the forest gap. $CaCO_3$ is the primary buffer substance for acidity and is consumed to a higher degree in the uppermost few centimetres of the forest soil.

The higher litter input in the forest and the slower and incomplete mineralisation of the beech litter leads to an approximately three times higher organic matter content of the forest topsoil compared to the topsoil of the forest gap. This difference is also apparent in the subsoil even though on a lower level.

4.2 Effect of tree canopy and litter on throughfall and litterflow chemistry

We have shown significant differences in element fluxes in throughfall of Oriental beech forests compared to rainfall for all four elements analysed. Throughfall chemistry is mainly affected by the washing of deposits from the canopy surface, by leaching elements from internal plant tissues and through the uptake of elements in the canopy (Potter 1991). Many studies in the literature have demonstrated higher amounts of Na^{+}, K^{+}, Ca^{2+} and Mg^{2+} in throughfall compared to rainfall amongst all different climates and forest types (Potter 1991; Chuyong et al. 2004; Tobón et al. 2004a; Duchesne and Houle 2006; Dezzeo and Chacón 2006; Ndakara 2012; Adedeji and Gbadegesin 2012). From all measured cations in our study, the amount of K^{+} in throughfall was the highest and Mg^{2+} the lowest ($K^{+} > Na^{+} > Ca^{2+} > Mg^{2+}$) which agrees with findings from previous studies (Staelens et al. 2003; André et al. 2008; Van Stan et al. 2012, Habashi et al. 2019). During the observation period, 54.6 kg K^{+} ha^{-1} entered the canopy layer of the beech forest while more than double this amount entered in the throughfall. The large amount of K^{+} in throughfall is attributed to the higher susceptibility of this cation to canopy leaching compared to Na^{+}, Mg^{2+} and Ca^{2+} (Staelens et al. 2003; André et al. 2008). This susceptibility is the result of the high mobility and leachability of K^{+} in cells near leaf surfaces (Schlesinger 1997; Tobón et al. 2004a), and the fact that it is not tightly bound in structure tissues or enzyme compounds (Draaijers et al. 1996).

Sodium in throughfall is often attributed to atmospheric deposition mainly from sea spray (Parker 1983). Our site is 50 km from the Caspian Sea and it is reasonable that the high amount of Na^{+} in rainfall (26.3 kg ha^{-1} $year^{-1}$) originates from this source. Furthermore, the additional 16.8 kg Na^{+} ha^{-1} $year^{-1}$ in throughfall is attributable to the washing of deposits accumulated on the canopy between precipitation events (Parker 1983; Devlaeminck et al. 2005) and only to a very small degree to canopy leaching, because Na^{+} is only found in low concentrations in leaves (Parker 1983).

Enrichment of Ca^{2+} and Mg^{2+} in throughfall after passing through the forest canopy was 18.6 and 2.9 kg ha^{-1} $year^{-1}$, respectively, increasing the amount of these cations in throughfall by a factor of 2.9 for Ca^{2+} and 1.9 for Mg^{2+} compared to rainfall. This is considerably more Ca^{2+} and less Mg^{2+} than Rothe et al. (2002) reported in a comparison of 16 biogeochemical studies in European beech (*Fagus sylvatica*) stands. They found across all sites, respective factors of 1.9 for Ca^{2+} and 3.4 for Mg^{2+}. The abovementioned enrichment factor for Mg^{2+} in our study is comparable to the other cations, with Ca^{2+} being somewhat higher. The leached amounts of Ca^{2+} and Mg^{2+}, on the other hand, are considerably lower compared to Na^{+} and K^{+}. Calculated on a molar basis, there were only 0.46 kmol Ca^{2+} ha^{-1} $year^{-1}$ and 0.12 kmol Mg^{2+} ha^{-1} $year^{-1}$ leached from the canopy compared to 1.5 kmol K^{+} ha^{-1} $year^{-1}$. This indicates the lower mobility of Ca^{2+} and Mg^{2+} which is due to the binding of Mg^{2+} in organic molecules, especially chlorophyll, and the fact that Ca^{2+} is an important constituent of the plant cell wall

(Kramer and Kozlowski 1979). Mainly for Mg^{2+}, dry deposition may supply more than 80% to the net throughfall in marine environments (Parker 1983) and the contribution of leaching is less important. This also applies, although to a lesser extent, to Ca^{2+}, given the much lower Ca^{2+} to Cl^- ratio in seawater (e.g. Krumgalz 1982; Nessim et al. 2015).

Throughfall is one important pathway through which base cations reach the forest floor, thus affecting the biogeochemical cycling of forested ecosystems (Augusto et al. 2002). A further significant process is litterfall and the leaching of the litter layer, which import base cations into the mineral soil (Moslehi 2010; Shabani 2013). We have shown that, with the exception for Na^+, all fluxes of base cations in litterflow are higher compared to rainfall, although the differences are only statistically significant for Ca^{2+}. In contrast, the fluxes of all measured base cations in litterflow were significantly smaller compared to throughfall. With our sampling design, one can assume that rainfall passes through the canopy layer, a part of rainfall enters the litter layer as throughfall and reaches the mineral topsoil as litterflow. While the base cation fluxes increase in throughfall compared to rainfall, they decrease by passing through the litter layer. This decrease can be ascribed to mainly two processes in the litter layer. The litter layer is biologically the most active layer where soil fauna and microorganisms meet their requirements through the uptake of essential base cations (Golley et al. 1975; Moslehi 2010; Shabani 2013). Besides this biological immobilisation, there is also adsorption of base cations to active surfaces in the litter layer. Obviously, these sinks for base cations are more pronounced than the sources of base cations which are released by desorption and mineralisation. The quantity of leached base cations depends not only on these processes but also on the amount of water percolating through the ecosystem layers. While 73% of rainfall passes through the canopy layer, there is only 32% of rainfall or 45% of throughfall leaving the litter layer. A large quantity of water is retained in the litter layer, and, in addition, water is partly evaporated. The evaporation of water additionally increases the adsorption of base cations in the litter layer (Moslehi 2010). Considering the individual cations in litterflow, K^+ was the dominant cation in litter leachates followed by Na^+, Ca^{2+} and Mg^{2+}, which coincides with the composition of throughfall and with findings from other regions in the world (Fujinuma et al. 2005; Johnson-Maynard et al. 2005). Considering the interaction of base cations with the surfaces of the solid phase in the litter layer, Ca^{2+} and Mg^{2+} are more tightly adsorbed compared to K^+ and Na^+ (Evangelou and Phillips 2005). Furthermore, base cations are also leached from the decomposing litter (Duivenvoorden and Lips 1995; Tobón et al. 2004a), and by means of faster decomposition, more abundant base cations preferably enter the soil by litterflow (Strobel et al. 2001; Van Nevel et al. 2013). The exchange and leaching of base cations depend on the chemical composition of the plant litter and the concentrations of the individual base cations in the litter (Eaton et al. 1973). Higher leaching of K^+ in litterflow can be explained by its high mobility and leachability in dead and living plants (Tobón et al. 2004b). Amini (2009) found the substantial release of K^+ from new fallen leaf litter of Oriental beech by decomposition. Approximately 80% of the K^+ in newly fallen leaf litter is released in the first month (Chuyong et al. 2002) while Ca^{2+} accumulates in the leaf litter during the first 2 years and is slowly released afterwards (Yavitt and Fahey 1986). Therefore, lower Ca^{2+} and Mg^{2+} than K^+ in litterflow leaching can likely be ascribed to (i) their lower concentrations in the leaf litter than K^+ (Duivenvoorden and Lips 1995), (ii) slower release of Ca^{2+} and Mg^{2+} during litter decomposition (Yavitt and Fahey 1986) because of tight bonding in structural tissues or enzyme complexes in comparison to K^+ (Campo et al. 2000), (iii) uptake by decomposers and immobilisation of Ca^{2+} and Mg^{2+} in their microbial biomass (Golley et al. 1975) and (iv) stronger adsorption of divalent Ca^{2+} and Mg^{2+} to the solid phase in the litter layer compared to the monovalent K^+ (Evangelou and Phillips 2005).

Sodium is often considered to be delivered entirely by atmospheric deposition, and to pass through the ecosystem with relatively small amounts being cycled by plants and soil biota (Verstraeten et al. 2012). In accordance with the proximity of the study area to the Caspian Sea, lower levels of Na^+ in leaves and a more considerable role played by marine depositions in Na^+ leaching are expected. Thus, the reduction of Na^+ leaching in litterflow relative to throughfall cannot be explained by biochemical processes.

4.3 Effect of canopy and litter on mineral soil solution

Our results indicate a higher load of K^+, Na^+ and Mg^{2+} in the forest soil solution compared to the forest gap, whereas for Ca^{2+}, the opposite is true. The interactions between soil solution and solid phase are different for the various cations and soil depths. The amounts of K^+ and Mg^{2+} leached from the topsoil and subsoil are greater in the forest compared to the forest gap by a factor of 1.4 to 2.4, although the differences are only significant for K^+ at both soil depths. This can mainly be attributed to canopy leaching and the considerable increase in a load of water percolating through the vegetation layer. The higher amount of water percolating through the soil in the forest compared to the forest gap (408 mm vs. 327 mm in topsoil, 336 mm vs. 239 mm in subsoil) may also partly explain the higher leaching of base cations in the forest. These differences in the amount of percolating water could be attributed to the highly varying slope of the site (35% in average) and the high amount of clay in the subsoil which leads to lateral water flow with high spatial variability. The higher amount of percolating water in the topsoil of the forest compared to the litter layer may similarly be explained. In the litter layer, the horizontally layered leaves may lead to an even higher lateral flow with huge spatial variability.

In the case of K^+, 65.8 kg ha^{-1} $year^{-1}$ enters the top mineral soil as litterflow in the forest, whereas in the forest gap the K^+ input to the topsoil by rainfall only amounts to 54.6 kg ha^{-1} $year^{-1}$, a difference of 11.2 kg^{-1} ha^{-1} $year^{-1}$. This difference increases to 18.7 kg ha^{-1} $year^{-1}$ in the water leaving the topsoil (TSF-TSO) and still amounts to 16.3 kg ha^{-1} $year^{-1}$ in the water leaving the subsoil (SSF-SSO). The transfer coefficients between water input and topsoil, calculated as the ratio of TSF/LF for the forest and TSO/RF for the forest gap, are both very similar (0.7 for the forest and 0.6 for the forest gap), meaning that the extent of the interactions between percolating water and topsoil are similar for both areas. The same is true for the topsoil–subsoil transfer coefficients. Transfer coefficients lower than 1 mean that K^+ disappears from the soil solution by passing through the mineral topsoil. Potassium adsorbs to the soil surface and/or is taken up by the vegetation and soil fauna. Potassium is a highly mobile base cation in forests, which cycles easily between the soil and vegetation (Frank and Stuanes 2003). However, the older the organic matter is, the less K^+ will be released to the soil water. As mentioned above, K^+ is easily leached from living plant material and 80% of K^+ from the litter is released during the first month (Chuyong et al. 2002). Therefore, the sinks which remove K^+ from the soil solution (mainly adsorption and biological fixation) dominate the sources which supply K^+ to the soil solution (mainly desorption and leaching of soil organic matter) in both the topsoil and the subsoil of the forest and the forest gap.

The dissolved Mg^{2+} behaved in the aboveground part of the Oriental beech forest similarly to Ca^{2+}. Magnesium is enriched in litterflow compared to rainfall by a factor of 1.4 due to canopy leaching, which means that 4.5 kg Mg^{2+} ha^{-1} $year^{-1}$ enter the topsoil in the forest compared to 3.2 kg ha^{-1} $year^{-1}$ in the forest gap (a difference of 1.3 kg ha^{-1} $year^{-1}$). This difference increases steadily to 2 kg ha^{-1} $year^{-1}$ in the topsoil and 3.8 kg ha^{-1} $year^{-1}$ in the subsoil. The amount of leached Mg^{2+} increases from the litter layer to the topsoil. While the transfer coefficients in the topsoil are similar for the forest and the forest gap, more Mg^{2+} is leached in the forest in terms of absolute quantities. The transfer coefficients are higher than 1, which means that Mg^{2+} is released to the soil solution in the top mineral soil. On average, the molar concentrations of Mg^{2+} in rainfall, litterflow and the soil solution of topsoils were 2×10^{-5} Mol L^{-1}, 6×10^{-5} Mol l^{-1} and 8×10^{-5} Mol L^{-1}, respectively. The respective concentrations for K^+ were 1.4×10^{-4} Mol L^{-1}, 5.3×10^{-4} Mol L^{-1} and 3.0×10^{-4} Mol L^{-1}, respectively (data not shown). The much lower concentrations of Mg^{2+} mean that in contact with the mineral soil, a new equilibrium is established which tends to desorb Mg^{2+} with greater likelihood than K^+ due to the concentration differences. Furthermore, Ca^{2+} and Mg^{2+} are more strongly bound in plant cells and, during decomposition, they accumulate in the leaf litter during the first 1 to 2 years and thereafter are slowly released (Yavitt and Fahey 1986). This points to older litter and organic matter in the topsoil of the forest as a continuous source of Mg^{2+} released to the soil water. This is also mirrored in the subsoil of the forest where higher amounts of organic matter are responsible for the greater leaching of Mg^{2+} compared to the forest gap, although the transfer coefficients SS/TS are less than 1.

The enrichment of Ca^{2+} in litterflow compared to rainfall by a factor of 1.5 due to canopy leaching means that 14.2 kg ha^{-1} $year^{-1}$ enter the topsoil in the forest compared to 9.5 kg ha^{-1} $year^{-1}$ in the forest gap (a difference of 4.7 kg ha^{-1} $year^{-1}$). In contrast to K^+ but similar to Mg^{2+}, the transfer coefficients for Ca^{2+} between water input and topsoil are higher than 1 (2.6 for the forest, 6.0 for the forest gap). The increase in dissolved Ca^{2+} in the soil solution of the topsoil is mainly due to the carbonate content in the soil (Schlesinger 1997), which is distinctly higher in the forest gap topsoil. In the forest subsoil, the leached amounts of Ca^{2+} are similar to those in the topsoil, while in the forest gap, they are reduced to 60% of the amount in the topsoil. The reason for this could be adsorption or precipitation of calcium, uptake of Ca^{2+} by soil fauna and vegetation (Swift and Anderson 1989), or a loss of Ca^{2+} by lateral water flow. Berger et al. (2009a, b) showed that nutrient leaching through the soil is not simply a ‘wash through’ but is mediated by a complex set of reactions within the plant-soil system.

Other than for the elements K^+, Ca^{2+} and Mg^{2+}, the plant demand for Na^+ is small, and the interaction between solution and soil surfaces is weak. Therefore, this element could be seen as a more or less inert tracer, and the ratios and transfer coefficients between the various layers are possibly symptomatic of the uncertainty in the experimental design, with the exception of the enrichment in throughfall, which can be interpreted as leaching of deposited Na^+ during rain-free periods.

4.4 Conclusions

From the comparison of water fluxes in an Oriental beech forest to those in an unforested gap nearby, it can be inferred that base cation quantities and fluxes are considerably greater in throughfall and litterflow in Oriental beech forests, which imply that these are important pathways for base cation inputs into the soil. Larger amounts of base cations in throughfall are caused by canopy exchange processes and atmospheric deposition from the Caspian Sea.

While base cation fluxes are greater in throughfall compared to rainfall, they decrease when passing through the litter layer due to biological immobilisation and physicochemical adsorption. Water evaporation from the litter layer further increases the adsorption of base cations in the litter layer. In the mineral soil, differences in leached quantities of base cations are mainly due to stronger adsorption of divalent compared to monovalent cations and different leachability and release during decomposition of organic matter.

Our results show that in the process of base cation cycling, Oriental beech trees return considerable amounts of these elements to the soil by throughfall and litterflow, and in this way help to maintain the soil fertility and forest sustainability. Amongst throughfall, litterflow, topsoil and subsoil, the contribution of throughfall to biogeochemical cycling is considerable, and thereby plays a key role in the biogeochemical cycle and plant growth. Thus, when selection cutting, timber marking and thinning, forest managers must consider the return of base cations through throughfall and litterflow in Oriental beech forests in order to account for their role in the nutrient cycling and sustainable nutrition of forests.

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Data availability The datasets generated and/or analysed during the current study are available in the EnviDat (www.envidat.ch) database (Moslehi et al. 2019) at https://doi.org/10.16904/envidat.66.

Compliance with ethical standards

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

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