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## SEASONAL CHANGES IN WATER CHEMISTRY IN A BOG ON THE SOUTHERN ALPS

Kasvukautiset vaihtelut pohjoisitalialaisen suon vesikemiassa

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Concentrations of sodium, potassium, calcium and magnesium were periodically measured in precipitation and in pool water in a bog on the Southern Alps during the 1991 vegetative season. A simple model was established for calculating theoretical concentrations of those cations in bog water, taking into account the effect of potential evapotranspiration. The actual concentrations of cations in bog water were then compared with the theoretical ones and this allowed to define different seasonal patterns of cation concentrations. Sodium accumulated in bog water with respect to precipitation, to an extent far exceeding the enrichment due to evaporation. A possible explanation of this resides in a surface enrichment owing to capillary flow. Potassium, and to a lesser extent magnesium, accumulated in spring and autumn but were actively removed by plants in summer. Calcium was removed also outside the growing season, probably by cation exchange on peat.

Keywords: bog water, cations, evapotranspiration, precipitation, seasonal variation.

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### INTRODUCTION

Ombrotrophic bogs are nutrient-deficient habitats, as they depend solely on the atmosphere for their supply of inorganic elements (Malmer et al. 1992). Periodical changes in the concentrations of major cations in bog pools and rainfall let us know the different behaviour of cations in bog habitats. Inorganic elements are either relocated or removed, depending on the hydrological conditions of bog microsites, by two different mechanisms, viz.: 1) uptake by vegetation and 2) adsorption on the cation-

exchange complex of the peat. The amount of cations removed depends on the chemical characteristics of each cation and on the metabolic processes in which that cation is involved (Damman 1978, Malmer 1988).

Damman (1988) outlined the following main seasonal trends for the major cations occurring in bog waters: 1) Sodium is poorly removed due to the low biological demand for this element. Sodium concentrations in bog water are usually far higher than in precipitation, mainly as an effect of evapotranspiration. 2) Potassium is actively removed by plants, so that its

concentration in bog water is lowest during the growing season when it falls below that in precipitation. 3) Calcium is removed mostly by adsorption on the cation exchange complex of the peat. As a consequence, calcium concentration in bog water is always lower than in precipitation with only minor seasonal changes. 4) Magnesium concentrations in bog water are usually higher than in precipitation. Magnesium is removed more actively than sodium, but less than calcium and potassium. Evapotranspiration tends to increase its concentration in bog water.

This paper aims at studying bog-water chemistry in a region where mire hydrology and hydrochemistry are poorly known. The seasonal patterns of variation in cation concentrations are related to precipitation chemistry by means of a simple model accounting for the enrichment due to evapotranspiration.

## MATERIAL AND METHODS

### Site description

The field study was performed at a small ombrogenous bog located on the Sarntaler Alpen (Monti Sarentini), province of Bolzano (Bozen) Italy, at 1 730 m. Climate is temperate-continental with mean annual temperature of 4.3°C, mean temperature of the coldest month (January) of -3.2°C, mean temperature of the warmest month (July) of 14°C, and average total rainfall of 909 mm. Precipitation usually peaks in late Spring-early Summer (Fliri 1975).

The vegetation of the bog consists of three main plant communities, corresponding to different microhabitats: high hummocks having *Sphagnum nemoreum* Scop. and *Polytrichum strictum* Menz. ex Brid. as dominant mosses, and *Calluna vulgaris* (L.) Hull. and *Vaccinium vitis-idaea* L. as dominant dwarf shrubs; low hummocks with *Sphagnum magellanicum* Brid. as dominant moss species and several graminoids in the field layer; mud-bottom hollows having *Scheuchzeria palustris* L. and *Carex limosa* L. as most distinctive character species. The outer sector of the bog is covered by a narrow belt of *Pinus mugo* Turra and *Picea excelsa* (Lam.) Link.

### Field work

Field work was carried out during the 1991 vegetative season. Six pools having comparable vegetation have been chosen; these pools are not influenced by mineral-soil water. At every pool a plastic pipe was inserted into the peat with the apex at the level of the bog surface. The plastic pipes consist of plastic polyvinyl chloride (PVC) casings with an inside diameter of about 1.5 cm and a wall thickness of about 2 mm. Water enters the pipe through lateral openings. Water levels were measured with a water-table gauge.

The depth of water table was measured and water samples from all pools were collected at intervals of  $20 \pm 1$  days from 21 May to 7 October. Rainfall was sampled in a glass rain-gauge. All water samples were stored in polythene bottles and deep frozen until analysis.

### Chemical analyses

The water samples were analyzed for  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  by atomic absorption spectrophotometry. Lanthanum was added to the samples analyzed for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  to reduce anionic interference.

### Statistical treatment

For every interval into which the study period was divided, the mean depth of water table was measured and the mean cation concentrations were calculated both for pool water and for precipitation. The daily potential evapotranspiration was calculated with Hamon's formula (1) (Hamon 1963):

$$\text{ETP} = 0.165 * c * U \quad (1)$$

where  $c$  = ratio of daylength with that of the conventional day (i.e. 12 hours)

$U$  = tension of saturated vapor which is function of the mean daily temperature.

Theoretical concentrations (as  $\mu\text{eq l}^{-1}$ ) of cations in pool water at the  $t$ -time ( $\text{TC}_t$ ) were calculated with the following formula:

$$\text{TC}_t = (A_t - B_t) / C_t \quad (2)$$

with:

$$A_t = \alpha_0 * (D + h_0) + \sum_{i=1}^t P_i * R_i - \sum_{i=1}^t B_{i-1} \quad (3)$$

$$B_i = (PN_i W_i) * ((A_i / (P_i + D + h_i)) + (A_i / (PN_i + D + h_i))) / 2 \quad (4)$$

$$C_t = D + h_0 + \sum_{i=1}^t W_i \quad (5)$$

and:

$$PN_t = P_t - ETP_t \quad (6)$$

where:

$\alpha_0$  = mean concentration on 21 May in bog water ( $\mu\text{eq l}^{-1}$ )

$h_0$  = mean depth of water table on 21 May (mm)

$D$  = depth of acrotelm (mm); in this study  $D$  was set equal to the maximal depth of water table recorded in all bog pools over the sampling period (viz. 140 mm)

$P_i$  = rainfall in the  $i$ -th interval (mm)

$ETP_i$  = (potential) evapotranspiration in the  $i$ -th interval (mm)

$R_i$  = mean concentration in rain water in the  $i$ -th interval ( $\mu\text{eq l}^{-1}$ )

$W_i$  = increment of water table level in the  $i$ -th interval (mm)

$h_i$  = mean water table depth on the  $i$ -th recording date (mm).

## RESULTS

Precipitation was most abundant in June with a secondary peak in October. A long dry period lasted from the beginning of August till mid-September. Potential evapotranspiration (ETP) reached its highest values in July and early August. The difference between rainfall and ETP was greatest in the period between mid-August and mid-September (Fig. 1).

In precipitation, the concentrations of  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$  abruptly decreased all over the summer. Instead,  $\text{Ca}^{2+}$  concentrations decreased more gradually. There was no input of elements in the period 8 August – 15 September owing to the lack of precipitation (Table 1).

In bog water, the concentrations of  $\text{Na}^+$  were higher than those of the other cations, with little variation among pools and greater variation among periods. The concentrations of  $\text{K}^+$  showed a great internal variation as a result of marked differences among pools. Variation was smaller among periods. The concentrations of  $\text{Ca}^{2+}$  showed a seasonal pattern comparable to that of  $\text{Na}^+$ , but with lower concentrations. The concentrations of  $\text{Mg}^{2+}$  were remarkably constant both among periods and among pools (Table 2).

$\text{Na}^+$  was always much more concentrated in bog water than in precipitation;  $\text{K}^+$  and  $\text{Ca}^{2+}$  were more concentrated in precipitation than in

bog water only until the end of June;  $\text{Mg}^{2+}$  was more concentrated in bog water with the only exception of 11 June.

The real concentrations of  $\text{Na}^+$  in pools were somewhat lower than the theoretical concentrations only until the end of June. Later on, the real concentrations were far higher than the theoretical ones (Fig. 2a). The theoretical concentrations of  $\text{K}^+$  were always higher than the real ones until mid September. Only at the end of the growing season did this trend invert (Fig. 2b). The real concentrations of  $\text{Ca}^{2+}$  were always lower than the theoretical ones, the greatest difference between the two curves being in July (Fig. 2c). The theoretical concentrations of  $\text{Mg}^{2+}$  were higher than the real ones until mid August. Then the differences decreased and in October the real concentration exceeded the theoretical one (Fig. 2d).

## DISCUSSION

Estimates of ETP based on current meteorological data are largely employed in hydrologic modelling as they often provide satisfactory results in the absence of experimental records of actual evapotranspiration (Saxton & McGuinness 1982). On the other hand, there is some evidence that the actual evapotranspiration from bogs is approximately equal to potential evapotranspiration (Ingram 1983). Hamon's (1963) formula was chosen among the various

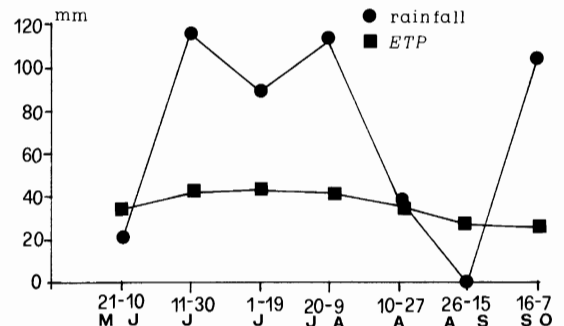


Fig. 1. Seasonal pattern of rainfall and potential evapotranspiration.

Kuva 1. Kasvukautinen sateen ja potentiaalisen haihtumisen kehitys.

Table 1. Mean concentration ( $\pm$  S.E.) of cations in the precipitation of each interval. Data as  $\mu\text{eq l}^{-1}$ .Taulukko 1. Tutkittujen kationien keskiarvot ja standardipoikkeamat tutkimusvälien aikana. Arvot  $\mu\text{eq l}^{-1}$ .

	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>
4–10 June	30.1 $\pm$ 15.1	21.0 $\pm$ 2.0	50.4 $\pm$ 19.8	16.6 $\pm$ 8.2
11–30 June	15.5 $\pm$ 7.1	12.3 $\pm$ 3.9	57.5 $\pm$ 35.2	30.5 $\pm$ 27.2
1–19 July	8.0 $\pm$ 12.0	4.7 $\pm$ 9.5	44.3 $\pm$ 38.6	14.7 $\pm$ 12.8
20 J–9 August	6.0 $\pm$ 4.0	0.5 $\pm$ 0.7	30.4 $\pm$ 11.7	8.3 $\pm$ 2.6
10–27 August	3.5 $\pm$ 3.0	0.5 $\pm$ 0.7	20.7 $\pm$ 0.7	5.8 $\pm$ 0.0
28 A–15 September	0.0	0.0	0.0	0.0
16 S–7 October	11.0 $\pm$ 10.0	1.8 $\pm$ 2.5	48.3 $\pm$ 35.3	15.8 $\pm$ 13.0

Table 2. Mean concentrations ( $\pm$  S.E.) of cations in bog pools on each sampling date. Data as  $\mu\text{eq l}^{-1}$ .Taulukko 2. Tutkittujen kationien pitoisuudet (keskiarvo ja standardipoikkeama) kuljujen vedessä keräyspäivinä. Arvot  $\mu\text{eq l}^{-1}$ .

	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>
21 May	77.5 $\pm$ 25.3	21.3 $\pm$ 10.1	40.1 $\pm$ 8.9	23.2 $\pm$ 3.2
11 June	57.6 $\pm$ 20.6	7.3 $\pm$ 5.1	37.7 $\pm$ 26.1	19.7 $\pm$ 7.9
1 July	53.7 $\pm$ 11.8	6.6 $\pm$ 7.5	53.8 $\pm$ 10.9	25.0 $\pm$ 3.2
20 July	54.2 $\pm$ 14.9	6.2 $\pm$ 1.6	58.6 $\pm$ 22.3	27.2 $\pm$ 7.6
10 August	74.3 $\pm$ 25.1	6.2 $\pm$ 5.0	55.7 $\pm$ 18.9	26.7 $\pm$ 6.2
28 August	84.2 $\pm$ 23.4	11.0 $\pm$ 6.0	67.4 $\pm$ 26.3	30.7 $\pm$ 8.1
16 September	89.2 $\pm$ 20.8	9.9 $\pm$ 2.7	68.7 $\pm$ 32.5	32.2 $\pm$ 11.9
7 October	63.8 $\pm$ 6.9	12.6 $\pm$ 8.6	55.7 $\pm$ 19.6	32.0 $\pm$ 9.1

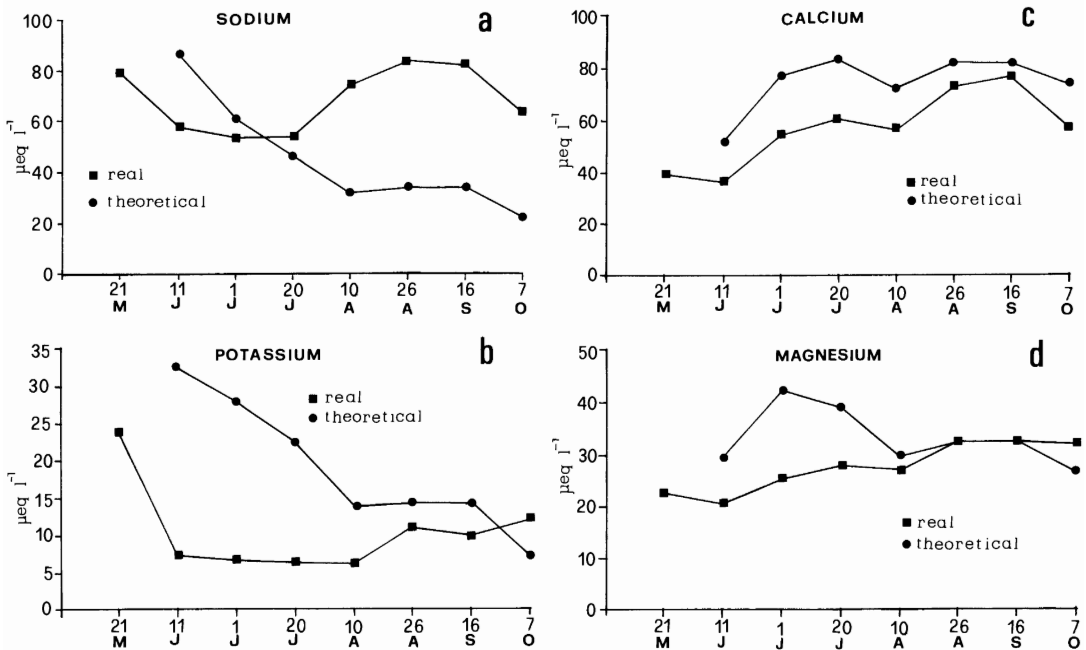


Fig. 2. Seasonal patterns of cation concentrations in bog water.

Kuva 2. Tutkittujen kationien kasvukautiset pitoisuuden vaihtelut. Kuvaan on merkitty sekä todellinen mitattu että laskettu potentiaalinen pitoisuus.

methods available because it performed well in estimating ETP from several montane areas in the southern Alps (Cazorzi et al. 1987).

The theoretical model employed in this study can be thought of as a reservoir which had reached its ionic equilibrium outside the growing period. Subsequently, the ionic concentrations may vary because of: a) input by precipitation; b) active relocation by root uptake and/or sequestering in the peat; c) output by draining water. Hence, the theoretical concentrations are calculated by a stepwise procedure, viz. by adding on every interval the contributions and the removals which occurred in all of the previous intervals.

The model assumes that seepage remove cations only by lateral movement in the acrotelm, for water movement through the catotelm being exceedingly slow, due to the low hydraulic conductivity, and therefore negligible (Ivanov 1953, Boelter 1965). The model further assumes that the thickness of the acrotelm in the hollows be equal to the maximal water table depth recorded among all sampling sites. When  $PN_t$  is negative, it is set equal to zero. The mean cation concentration in draining water is calculated (formula (4)) as an average between two extreme concentrations, viz. that referred to the real rainfall (P) and that referred to the net rainfall (PN) respectively.

This model suffers some severe limitations, mainly consisting in the lack of data on plant uptake and lateral water-flow as well. Both could not be regrettably acquired in this study. Nonetheless, three main different situations can be grossly outlined for a given cation. First, the theoretical concentration is equal to the real one: this means that the cation is not taken up by vegetation, either by root absorption or by ionic exchange on the peat, but is removed only by lateral movement of water. Second, the theoretical concentration is higher than the real one: this means that the cation is taken up besides being removed by draining water. Third, the theoretical concentration is lower than the real one: this means that there is an additional input of this element besides that of rainfall.

The higher theoretical concentration of sodium in June (Fig. 2a) was probably determined by spring rainfall of oceanic origin which is unusually rich in this cation (Table 1). Subsequently, the real concentration of sodium largely exceeded the theoretical one as a possible

consequence of a surface enrichment by capillary flow and evaporation (Brehm 1971, Damman 1986). A reversal in the hydraulic gradient can also play a role in this respect (Siegel & Glaser 1987). On the other hand, segregation and immobilization of  $Na^+$  in the top peat layer determined by overlying freezing water (Kadlec et al. 1988) do not seem to be effective for enriching sodium in bog water. If ETP is calculated based on the ratio: Na concentration in bog water/precipitation, and the expected concentrations of other cations are obtained by multiplying their concentration in precipitation with that ratio (Boatman et al. 1975, Damman 1986), the latter concentrations may be considerably overestimated.

The theoretical concentrations of potassium (Fig. 2b) were distinctly higher than the real ones during the growing season. This means that potassium was actively absorbed by vegetation. In September the difference between the two concentrations was smaller, owing to the slowing down of vegetation growth at the end of the vegetative season. In October the real concentration was higher than the theoretical one as a probable effect of both the leachability of cryptogam tissues induced by senescence (Gerdol 1991) and by the high mobility of potassium (Malmer 1988).

Calcium was continuously removed during the sampling period (Fig. 2c). A relatively slow release during tissue senescence, for calcium being more stable than other cations, as well as adsorption of this cation on the exchange complex of peat (Damman 1986) play a major role in determining the seasonal trend of calcium concentrations in bog water.

Magnesium (Fig. 2d) was taken up by vegetation during the growing season; the real concentration of  $Mg^{2+}$  approached the theoretical one since half August because of the slowing down of vegetation growth. The peak of real concentration in October could be caused by senescence.

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## TIIVISTELMÄ:

## KASVUKAUTISET VAIHTELUT POHJOISITALIALAISEN SUON VESIKEMIASSA

Natriumin, kaliumin, kalsiumin ja magnesiumin pitoisuudet erään pohjois-italialaisen vuoriston (Monti Sarentini, 1730 m m.p.y.) kohosuon kuljuista sekä sateesta mitattiin n. kolmen viikon välein touko-lokakuussa 1991. Potentiaalista haihduntaa (ETP) apuna käyttäen muodostettiin yksinkertainen malli, jolla laskettiin tutkittujen alkuaineiden potentiaaliset pitoisuudet suovedessä. Vertaamalla laskettuja potentiaalisia ja mitattuja todellisia alkuaineiden pitoisuuksia suovedessä pystyttiin määrittämään tutkittujen kationien kasvukautisia pitoisuuden vaihteluja.

Natriumia oli suovedessä selvästi enemmän kuin sateessa. Haihdunnan pintaan rikastava vaikutuskaan ei pystynyt selittämään eroa. Luultavasti natriumia kulkeutuu kapillaarisesti suon pinnalle syvemmillä olevasta vedestä. Kalium ja pienemmässä määrin myös magnesium rikastuivat suoveteen keväällä ja syksyllä. Kesällä kasvillisuus otti niitä aktiivisesti, jolloin niiden pitoisuudet suovedessä laskivat. Kalsiumin pitoisuuden vaihtelut osoittivat, että sitä adsorboituu turpeen kationinvaihtosysteemiin.

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