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# Variation in groundwater composition and decalcification depth in a dune slack: effects on basiphilous vegetation

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Abstract. Basiphilous, open, species-rich vegetation types of young dune slacks have declined throughout Europe in recent years, and have largely been replaced by often acidophilous, tall marsh and scrub vegetation. This succession appears to be accelerated by a decrease in the discharge of calcareous groundwater from sandy ridges or small dune hummocks. The present study deals with spatial and temporal variation in the chemical composition of the groundwater in the upper metres of the soil of a degraded dune slack complex on the Dutch barrier island of Schiermonnikoog, with emphasis on (1) groundwater composition, (2) water level and (3) decalcification patterns. The main aim was to assess perspectives for restoring basiphilous vegetation types which had been abundant in this slack from 1954 to 1977. The depth of decalcification was related to former hydrological conditions along a transect of 200 m. Acidifying effects of rainfall were reflected in the chemical composition of the groundwater below small dune hummocks within the slack. Distinct precipitation water lenses, poor in dissolved ions, were formed under the dune hummocks during a wet period. This microtopography did not contribute to the discharge of calcareous groundwater to lowlying parts of the slack. Here, groundwater showed decreasing concentrations of the dissolved ions after a rain shower. Except for the peripheral sections of the slack – where upward seepage of groundwater (exfiltration) still occurs - infiltration conditions are now dominant in the slack. The consequences of the present hydrological conditions for restoration are briefly discussed.

**Keywords:** Alkalinity; Calcite saturation; Calcium carbonate; Hydrochemistry; Schiermonnikoog.

**Nomenclature:** van der Meijden et al. (1990) for vascular plants; Schaminée et al. (1995) for plant communities.

## Introduction

Studies of dune slack vegetation in The Netherlands have revealed a decline in the extent of low-productivity vegetation types characterized by mesotrophic basiphilous species and an increase in the area of high productivity types characterized by acidophilous taxa. These changes have been attributed to both natural and

anthropogenic causes (Grootjans et al. 1988, 1991; van Dijk & Grootjans 1993). Among the species most affected are *Littorella uniflora*, *Schoenus nigricans*, *Epipactis palustris*, *Dactylorhiza incarnata* and *Parnassia palustris*, all of which are characteristic of the dune slack communities *Junco baltici-Schoenetum nigricantis*, *Samolo-Littorelletum* and *Parnassio-Juncetum atricapilli*.

Grootjans et al. (1988) suggested that the considerable decline of basiphilous species in a large dune slack complex on the Dutch barrier island of Schiermonnikoog was related to the processes of acidification and organic matter accumulation in the low-lying wet parts, and decalcification in the drier parts. Additional research (Grootjans et al. 1991) revealed that a series of relatively dry summers appeared to postpone the replacement of basiphilous plant species with acidophilous plant species by retarding vegetation succession. A sudden shift occurred after a period with very wet summers. These studies also suggest that topsoil acidification is not caused by decalcification, but rather by replacement of calcareous groundwater with acid rainwater in the form of a rainwater lens (Grootjans et al. 1991; Stuyfzand 1993).

Grootjans et al. (1996) described the hydrological functioning of the western part of the slack as a flowthrough lake when flooded. Such a slack receives most of its water by exfiltration of calcareous groundwater along the up-gradient shoreline. This water proceeds as surface water and infiltrates again along the downgradient shoreline (cf. Born et al. 1979). This mechanism is essential for the supply of nutrients and acid neutralizing components such as HCO<sub>3</sub><sup>-</sup> (Kenoyer & Anderson 1989; Cook et al. 1991). Van Dijk & Grootjans (1993) suggested also that very small dune hummocks with a height of < 1 m could contribute to the discharge of calcareous groundwater onto low lying areas with decalcified topsoils: a local hydrological mechanism would buffer the pH of the topsoil of low-lying areas thus creating suitable conditions for basiphilous species.

The purpose of this study was to investigate the contribution of such small dune hummocks in the discharge of calcareous groundwater into low-lying areas. The study focuses upon hydrology and soil chemistry, with special reference to the influence of two small secondary dune hummocks in the slack: management practices are discussed for the restoration of basiphilous vegetation.

#### **Material and Methods**

## Study area

The study area is the eastern part of a 6.6 ha dune slack complex called 'Kapenglop' on the island of Schiermonnikoog (45° 29' N, 6° 09' E) in the Dutch part of the Wadden Sea (Fig. 1). The slack is surrounded by three dune ridges, 150 - 400 yr old (Isbary 1936) which enclosed the slack and prevented flooding by seawater. Since that time the slack has been influenced only by fresh water (Grootjans et al. 1991). Later on secondary blowouts arose, perhaps promoted by cattle grazing which occurred until 1955.

In the early 1950s Westhoff (in Westhoff & van Oosten 1991) found well-developed *Junco baltici-Schoenetum* and *Samolo-Littorelletum* communities in this area, with characteristic basiphilous pioneer species (Schaminée et al. 1995). Grootjans et al. (1991) estimated that these communities became established between 1930 and 1940, probably after intensive sand blowing. These communities were still present in 1964. The decline in many basiphilous and pioneer species was monitored on permanent plots from 1964 to 1987 by Grootjans et al. (1988, 1991). They found that the dry summers of 1975-1977, with a mean deviation of – 105 mm from the mean precipitation surplus (1954-1987), had a negative effect on the cover of basiphilous

and pioneer species, but that few species disappeared. This happened, however, between 1977 and 1987, when several relatively wet summers occurred, with an average deviation of + 125 mm from the mean (Grootjans et al. 1991).

The present study was conducted in two phases: (1) in 1987 along a transect of 200 m (transect AA') at the scale of the whole dune slack; (2) in 1991 along two transects of 25 m (transects aa' and bb') at the scale of small dune hummocks (Fig. 1). The 200-m transect was situated in the eastern part of the Kapenglop where basiphilous species are known to have persisted for a long time (Grootjans et al. 1988). One 25-m transect (aa') overlapped with part of the 200-m transect and was situated near a ridge at the edge of the dune slack, where discharge of calcareous groundwater could be expected (Grootjans et al. 1996), the other (bb') was situated in the centre of the dune slack where predominantly neutral hydrological conditions were likely to prevail.

## Sampling method and analytical procedures

#### Vegetation

Changes in the distribution of rare species were recorded in plots  $(2 \text{ m} \times 2 \text{ m} \text{ or } 3 \text{ m} \times 3 \text{ m})$  along the 200-m transect of Grootjans et al. (1988) in 1964 and 1987, using the Braun-Blanquet cover-abundance scale. Data from the same transect in 1964 were derived from Frijlink (1965). In 1991, plant species were recorded along the two 25-m transects in plots of 0.5 m  $\times$  0.5 m.

#### Groundwater composition and soil

The first groundwater samples were collected in August 1987 along transect AA', at depths of 0.2 - 0.3, 0.5 - 0.6, 0.9 - 1.0 and 1.4 - 1.5 m below the soil surface. After sampling, pH, temperature and electrical conductivity at

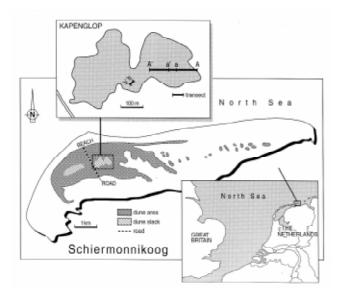


Fig. 1. Location of study sites and groundwater transects.

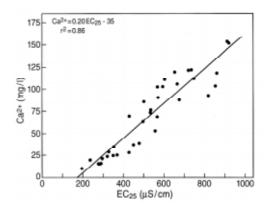
25 °C (EC<sub>25</sub>) were measured in the field. The concentrations of CO<sub>2</sub> (titration with 1M NaOH up to pH 8), HCO<sub>3</sub>concentrations (titration with 1M HCl down to pH of 4.5) and NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> were analyzed within 24 h of sampling. The samples were stored in the dark at 4 °C prior to further analysis. To prevent precipitation of instable cations, a 50 ml subsample was adjusted to pH 2 using 2.5 ml 4 % HCl. Ca, Mg, K and Na were analyzed directly using atomic absorbtion spectrometry. Cl-was analyzed by measuring the ferric-thiocyanate colour at 490 nm,  $SO_4^{2-}$  by measuring the methylthymol blue colour at 460 nm (Skalar). The charge balance and the EC<sub>25</sub> were calculated to check the reliability of the analyses. Inaccurate analyses (with > 5 % deviation of the charge balance) were disregarded or re-analyzed. The saturation index for calcite (SI<sub>a</sub>-index) was calculated from the temperature, EC, pH and Ca<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> concentrations (Stuyfzand 1989). Groundwater with a  $SI_c$ -index lower than -1.0 is considered undersaturated (aggressive), a SI<sub>c</sub> between – 1 and 0.3 indicates that the groundwater is in equilibrium with calcite, and when the SI exceeds 0.3, the water is considered to be supersaturated with calcite (Stuyfzand 1993).

Soil samples were taken at depths of 0 - 0.10, 0.10 - 0.20, 0.20 - 0.30, 0.50 - 0.60 and 0.90 - 1.00 m below the soil surface and analyzed for pH(H<sub>2</sub>O) by adding 20 ml of deionized water to 15 g of fresh soil. The remaining parts of the soil samples were dried at room temperature (25 °C) and ground to a maximum particle diameter of 2 mm. Samples pre-treated in this way were analyzed for CaCO<sub>3</sub> (HCl-Ca-method; 50 ml 1 N HCl added to 2.5 g soil). A CaCO<sub>3</sub> content of less than 0.1% was chosen as the uppermost threshold for decalcification.

In 1991, groundwater was sampled every week between 24 May and 27 July along transects aa' and bb'; groups of three piezometers were placed in clusters at intervals of 5 m. Sampling depths for the piezometers were 2.45 - 2.60 m, 2.20 - 2.30 m and 1.75 - 1.85 m above mean sea level (MSL). The samples were analyzed for pH and EC<sub>25</sub> in the field. All samples collected on 30 May were analyzed for EC<sub>25</sub> and Ca<sup>2+</sup> concentration in order to check for linear correlation – which amounted to 0.865 (Fig. 2). We concluded that EC<sub>25</sub> predicts the calcium concentration of the groundwater very well. Further EC<sub>25</sub> measurements of groundwater were continued for estimating the calcium concentration.

The soils of transects aa' and bb' were sampled in 1993 down to 2 m deep. The decalcification depth was checked in the field using a 10 % HCl solution: visible/audible effervescence was regarded as indicative of CaCO<sub>3</sub> presence. This method was used to select soil samples for subsequent precise analyses of CaCO<sub>3</sub> content.

Boundaries between groundwater and soil concentration zones were calculated using the interpolation program of GIS-ILWIS (Valenzuela 1988).



**Fig. 2.** Relationship between the electrical conductivity (EC $_{25}$   $\mu$ S/cm) and calcium concentration (mg/l) of shallow groundwater samples collected in 1991 along transects aa' and bb'.

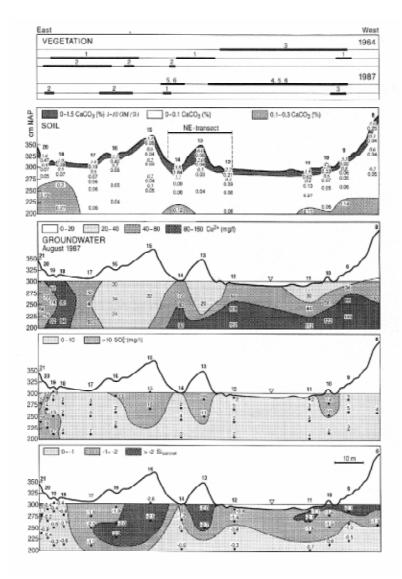
## Groundwater levels and weather conditions

Groundwater levels were measured along transects aa' and bb' immediately before the weekly collection of groundwater samples, from 24 May to 27 July 1991. Data from the Royal Dutch Meteorological Institute (Anon. 1991) were used to calculate the daily precipitation surplus (precipitation minus evapotranspiration). For this purpose, daily precipitation measurements from the weather station at Schiermonnikoog were used. Unfortunately evapotranspiration data were not available for Schiermonnikoog and so daily values were estimated from meteorological data collected at a nearby weather station (Lauwersoog) at the mainland some 10 km south of the island. The calculations were according to the method of Makkink desribed in de Bruin (1987).

#### Results

Vegetation

In 1964, basiphilous species such as *Schoenus nigricans* and *Epipactus palustris* occurred abundantly in the eastern part of transect AA' (Frijlink 1965), while *Pedicularis palustris* dominated the low-lying western part (Fig. 3a). However, in 1987 *S. nigricans* and *E. palustris* were only found in small numbers on the eastern part of the slack, while only one individual of *P. palustris* remained on the western slope. In 1991, *P. palustris* was the only basiphilous species recorded on the slopes of the hummocks (Fig. 4a). Species indicating relatively acid (*Potentilla erecta*) or dry (*Holcus lanatus*) conditions were frequently found on the higher parts of the hummocks. On the lower parts *Eleocharis palustris* and *Eriophorum angustifolium* were recorded, which are indicative of wetter and acidic conditions respectively.



**Fig. 3.** The distribution of plant species and soil and groundwater chemical variables along the transect AA', including the sample sites (bold numbers) in 1987.

- **a.** Presence of plant species; where 1 = Epipactis palustris, 2 = Schoenus nigricans, 3 = Pedicularis palustris, 4 = Eriophorum angustifolium, 5 = Potentilla palustris, 6 = Eleocharis palustris, 7 = Holcus lanatus, 8 = Potentilla erecta.
- **b.** Percentage calcium carbonate and organic matter (OM, shown in italics) content of the top 2.5 m of the soil profile. Note that the percentage CaCO<sub>3</sub> in the toplayer with organic matter, in fact represents exchangeable Ca from the exchange complex.
- c. Calcium content (mg/l) of groundwater.
- d. Sulphide concentration of groundwater (mg/l).
- e. Calcite saturation index (SI<sub>2</sub>) of groundwater.

Patterns of variation in CaCO<sub>3</sub> content

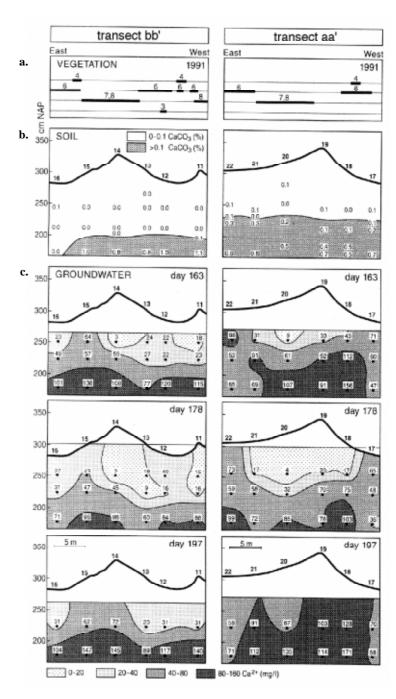
Soils along transect AA' were decalcified to a depth varying between 0.5 m (eastern periphery) down to more than 2.5 m below the soil surface (Fig. 3b). On most sites, the CaCO<sub>3</sub> boundary was at ca. 2 m above MSL. In 1991 a more detailed study of the two small hummocks showed that the decalcification depth did not follow the soil surface, but was nearly horizontal in both areas (Fig. 4b). The decalcification depth along the whole of transect bb' was at ca. 2.0 m above MSL and slightly lower than in transect aa'. The decalcification front in transect aa' was, however, sharper, with an increase in CaCO<sub>3</sub> content of almost 1 % over 0.50 m.

## Groundwater composition

In August 1987, the chemical composition of the groundwater showed small-scale variation along the 200-m transect (Fig. 3c). In the eastern part, groundwater rich

in Ca<sup>2+</sup> (> 40 mg/l) and SO<sub>4</sub><sup>2-</sup> (> 10 mg/l) was present up to the soil surface and showed no increase of concentration with depth. In other low-lying parts of the slack, the Ca<sup>2+</sup> concentration increased with depth. The groundwater was always Ca<sup>2+</sup>-rich (> 40 mg/l) but very poor in SO<sub>4</sub><sup>2-</sup> (< 10 mg/l). Groundwater with the lowest Ca<sup>2+</sup> concentrations (< 40 mg/l) and highest SO<sub>4</sub><sup>2-</sup> concentrations (> 10 mg/l) was found below the small dune hummocks. Shallow groundwater below the hummocks was calcite aggressive (SI-index < -2.0). In contrast, shallow groundwater in the eastern part and between the small hummocks was in equilibrium with calcite (SI<sub>c</sub>-index > -1; Fig. 3e).

In 1991, at day 163, the concentration of  $Ca^{2+}$  in the groundwater under the small hummocks was low (< 40 mg/l). After a wet period of 6 - 8 days, the  $Ca^{2+}$  concentrations decreased (shown at day 178; Figs. 4c and 5). High  $Ca^{2+}$  concentrations (> 40 mg/l) were found in the lower parts at day 163. After this wet period, the concen



**Fig. 4.** The distribution of plant species and soil and groundwater chemical variables along the transects aa' and bb', including the sample sites (bold numbers), in 1991.

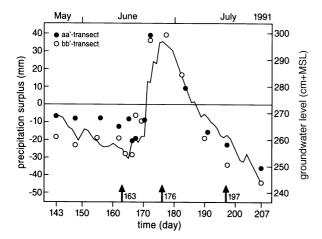
- a. Presence of plant species; where
- 3 = Pedicularis palustris,
- 4 = Eriophorum angustifolium,
- $5 = Potentilla \ palustris,$
- 6 = Eleocharis palustris,
- 7 = Holcus lanatus,
- 8 = Potentilla erecta.
- **b.** Percentage calcium carbonate over 1.5 m of the soil profile.
- **c.** Calcium content (mg/l) of groundwater estimated from  $EC_{25}$  values measured at day 163 (before a rain shower), at day 178 (during a rain shower) and at day 197 (after a rain shower).

tration of  $Ca^{2+}$  decreased (shown at day 178), followed by an increase which was similar to the situation before the rain shower at day 197.

## Groundwater levels and weather conditions

In May-July 1991, mean groundwater levels along transects aa' and bb' followed the pattern of the precipitation surplus: an increasing surplus resulted in an increasing groundwater level and *vice versa*. During periods of low precipitation surplus the mean groundwater level

along transect aa' was higher than along transect bb' (day 143 - day 172 and day 190 - day 207; Fig. 5). The ground-water levels at different depths per site were identical, independent of dry or wet periods, indicating that there was neither upward nor downward flow of groundwater (Fig. 6). Water levels between the transects, however, were different. During a dry period at day 163, groundwater levels along transect bb' were lower than in transect aa'. This pattern reversed during the wet period on day 184, with higher levels recorded along transect bb' (Fig. 6).

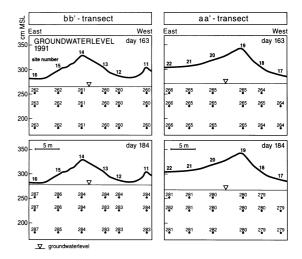


**Fig. 5.** The calculated precipitation surplus (mm, solid line) and mean groundwater level (cm +MSL) of transect aa' (black dots) and bb' (open dots).

#### Discussion

Hydrology related to decalcification depth

Carbonates present in the upper layers of calcareous dune soils gradually dissolve in areas with a precipitation surplus like in The Netherlands (van Breemen & Protz 1988; Stuyfzand 1993) and the topsoil is leached in the course of centuries (Olson 1958; Salisbury 1925; Rozema et al. 1985) or even decades (Wilson 1960). Spatial variations in decalcification depth are not only determined by spatial differences in precipitation surplus (van Breemen & Protz 1988), but also by variations in annual groundwater levels, which create differences in the vertical direction of groundwater flow (Stuyfzand 1993). Indeed Grootjans et al. (1996) and Sival & Grootjans (1996) found that decalcification had occurred at very shallow depths in an exfiltration zone of the western part of the Kapenglop, with deep decalcification noted in the infiltration zone. Predominant exfiltration of groundwater apparently slowed down decalcification, while pronounced infiltration led to intense leaching of the soil. The shallow depth of decalcification at the eastern periphery of transect AA' is probably also linked with exfiltrating groundwater. This explanation may, however, be only partly valid here. The almost horizontal decalcification front encountered at ca. 2.0 +MSL in various locations in the slack could have been formed centuries ago in an old beach plain. The limit of decalcification in the lowest parts is approximately 1 m, which is below the present mean lowest water level (ca. 0.50 m below the surface). Stuyfzand (1993) estimated a decalcification rate of 1.15 m per century for a Dutch dune area, poor in lime (0.2% CaCO<sub>3</sub>). For our study area, with an initial lime content of 1,2% CaCO<sub>3</sub> and with an infiltration flux of 0.75 mm day<sup>-1</sup>



**Fig. 6.** Piezometric levels along transect aa' and bb' during dry (day 163) and wet periods (day 184) in 1991.

(Anon. 1993), the decalcification rate would be 0.29 m per century, assuming a linear decalcification process under infiltration conditions. As the Kapenglop area is estimated to be 400 years old (Isbary 1936) the expected decalcification depth would thus be 1.16 m, which is very close to what we found. The decalcification beneath the hummocks and slack slopes is often much higher. These calculations support the idea that the micro-relief originates from secondary sand blowing of already decalcified sand. Differences in vertical groundwater flow patterns, which were partly the result of this change in micro-relief, have added to the differentiation of the old decalcification pattern in the soil.

All of the information presented here points to infiltration as the dominant process in the central areas of the slack, while exfiltration of groundwater has occurred at the eastern bordering zones.

Spatial variation in groundwater composition

The dissolution of CaCO<sub>3</sub> is predominantly reflected in composition of the groundwater in the Kapenglop area. Differences in Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> concentrations, however, yield little information on the origin of the groundwater (Schot & Wassen 1993). The origin of groundwater below the decalcified hummocks, however, is relatively easy to interpret: this water is calcium-poor but relatively sulphate-rich; it is derived from infiltrating rainwater. Rainwater in the coastal area generally has high amounts of sulphate (Stuyfzand 1993). Groundwater below the hummocks and the surrounding sandy ridges is aggressive towards CaCO<sub>3</sub> (low SI<sub>2</sub>-index). Deeper in the soil, the SI<sub>c</sub>-index increases due to the dissolution of CaCO<sub>3</sub>; the range of values between –1 and 0.3 indicates that the groundwater is in equilibrium with calcite. Hence the Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> concentrations rise.

At the eastern periphery of the slack the groundwater also has a high SI<sub>c</sub>-index and values are constant at all depths. This water is in equilibrium with calcite, but contains relatively high sulphate concentrations (SO<sub>4</sub><sup>2-</sup> >10 mg/l). We interpret this water as exfiltrating groundwater from the surrounding dune area, where groundwater levels are higher than in the Kapenglop (Grootjans et al. 1996). The high sulphate concentrations can be explained by the absence of organic matter in the subsoil of the surrounding dunes. Consequently hardly any sulphate is reduced when rainwater infiltrates in these areas, not even in deeper layers. When the groundwater discharges in the slacks, it has dissolved Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup>, but is still relatively rich in sulphate. Therefore, the groundwater composition in the soil profile at the eastern periphery of the slack indicates a predominantly upward flow of groundwater.

In contrast, the groundwater between the small hummocks and in the low-lying centre of the slack becomes increasingly saturated with calcite with depth, but sulphate is (nearly) completely reduced ( $SO_4^{2-} < 5 \text{ mg/l}$ ). This water probably originated from precipitation or surface water which had passed through the organically enriched topsoil. The interaction between this infiltrating water with the microbial populations in the decomposing biomass resulted in  $SO_4^{2-}$  reduction with  $HCO_3^{-}$ production and Ca<sup>2+</sup> release from the exchange complex (Wessel & Tietema 1995). In the rooting zone CO<sub>2</sub> was dissolved and the water became aggressive towards calcite. In deeper layers dissolution of calcite occurred and the water became saturated with calcite. The combined interpretation of calcium, sulphate and SI<sub>c</sub>-index patterns in the groundwater all point to the large-scale dominance of downward over upward water flow here.

Water in the centre of the slack is not just derived from precipitation, but also includes surface water from other parts of the slack. This became clear in 1991, when a steep increase in water level of ca. 0.35 m was measured in June (between days 163 and 178). The precipitation surplus of that period was ca. 50 mm and this should have resulted in a rise in groundwater level of 0.125 m, assuming a soil porosity value of 40 % (Stuyfzand 1993). Consequently the excessive rise in water level below the central hummock, must be largely due to surface water inflow from the surrounding area.

## Reconstruction of the flow-path pattern

During periods of flooding, it is thought that sulphate-rich, calcareous groundwater exfiltrates into the slack from the relatively large surrounding hydrological system (Fig. 7). This exfiltrating groundwater proceeds as surface water through the organically enriched topsoil layer and infiltrates again in the down-gradient part of the dune slack in a manner similar to that described for flow-through lakes (Born et al. 1979; Stuyfzand & Moberts 1987). For most of the year this calcareous groundwater remains in the decalcified subsoil and does not reach the topsoil, except for the eastern periphery where relics of basiphilous communities survive. The former abundance of basiphilous plant species (1964) over large parts of the slack suggest that the discharge of calcareous groundwater was once stronger, but since baseline data from that period are lacking this remains speculative.

Seepage of groundwater from the small dune hummocks, as suggested by van Dijk & Grootjans (1993), is unlikely. The groundwater at the slopes of the small dune hummock exhibited high concentrations of Ca<sup>2+</sup>, but these were still lower than the concentrations measured in exfiltrating groundwater at the periphery of the slack. These higher concentrations at the slopes of the hummocks are most probably a result of exchange reactions on the organic matter complex.

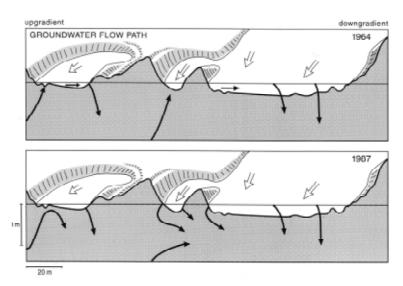


Fig. 7. Hypothetical groundwater flow pattern (black arrows) on a dune slack scale for 1964 and for 1987, based on groundwater chemistry and soil data collected along transect AA' in 1987. The open arrows represent surface water flow.

#### Implications for management

The reversal of acidification is only possible when H<sup>+</sup> is neutralized by acid buffering components such as bicarbonate (Kenoyer & Anderson 1989; Cook et al. 1991). The addition of calcareous groundwater not only reverses the effects of acidification but also restores base saturation following the displacement of Al and H by Ca<sup>2+</sup> and Mg<sup>2+</sup>. This process typically requires many years (Stuyfzand 1993).

A combination of measures is recommended to restore mesotrophic alkaline conditions. Mowing – used in the Kapenglop to prevent the development of tall herbs and grasses – has not prevented acidification (Grootjans et al. 1991). Sod removal reduces the amount of nutrients and H<sup>+</sup> production under dry soil conditions and decreases the distance between the soil surface and calcareous sediment. Restoring the conditions required by mesotrophic basiphilous vegetation is probably best achieved by rewetting; by increasing the groundwater input in combination with sod cutting.

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