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ON THE LIME TRANSITION AND DECALCIFICATION IN THE COASTAL DUNES OF THE PROVINCE OF NORTH HOLLAND AND THE ISLAND OF SCHIERMONNIKOOG

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SUMMARY

The transition zone between dunes rich and poor in calcium carbonate along a north-south and outer-inner dunes transect in the coastal dunes of the province of North Holland has been described.

The calcium carbonate content of the dunes from Wijk aan Zee (52°37′N,4°37′E) ranges from 1–10% in deeper layers (30–40 cm) with lower values in surface layers (0–10 cm). A more or less steep decrease in the calcium carbonate content has been observed in the area between with the milepost numbers 36 Egmond aan Zee and 32 Bergen aan Zee, from above 1% to far below 0.1% $CaCO_3$. The transition zone covers the Verbrande Pan area (mile posts 33 and 34) where BIJHOUWER (1926) located the border between the Waddendistrict (less than 1% $CaCO_3$ of the dry soil) and the Dunedistrict (more than 1% $CaCO_3$). It seems that the Waddendistrict has now extended southward to milepost 36 during the past 60 years.

Factors that influence the rate of decalcification in coastal dunes are discussed. A comparison is made between the carbonate leaching in the North Holland dunes and three differently aged dune systems on the island of Schiermonnikoog. The rate of decalcification in the Schiermonnikoog dunes did not significantly differ from that in the North Holland dunes, with a higher primary $CaCO_3$ content of the dune soil. Decalcification rates in surface layers of adjacent soils were found to differ due to the presence of a different vegetation.

1. INTRODUCTION

Variation of the $CaCO_3$ (lime, calcium carbonate) content in dune soils has been recognized as an important factor determining plant growth (RANWELL 1972). In the coastal dunes of The Netherlands, a sharp transition zone has been described between the phytogeographical "Waddendistrict" (poor in lime; $CaCO_3$ content of the dry soil less than 1% DW) and the "Dunedistrict" (rich in lime; 1–9% $CaCO_3$) (WESTHOFF 1947, DOING 1964). The better developed iron-film around sand-grains in the "Dunedistrict" causes the yellow-brown colour of the sand, while dunesand from the "Waddendistrict" is light-grey in colour.

The difference in the content of $CaCO_3$ between the "Waddendistrict" and the "Dunedistrict" seems to be primarily based on the more intensive deposition of shell-fragments in the dunedistrict (KLIJN 1981). The transition zone between the two phytogeographical areas is located between Egmond aan Zee (52°37′N, 4°37′E) and Bergen aan Zee (52°41′N, 4°41′E) (*figs. 4, 7*) (WESTHOFF 1947) and has been described in great detail nearly 60 years ago by BIJHOUWER (1926). Bijhouwer's study presents a well-documented phytogeographical and edaphic description of the "Verbrande Pan" area in particular. Despite extensive phytosociological and plant-ecological studies in this particular dune area, there are no more systematic studies of the soil characteristics of the dunes of North Holland available (BAKKER et al. 1979).

As part of a broader research programme aiming at the relationship between edaphic factors and the ecology of the dune ecosystem (ROZEMA 1978, ROZEMA et al. 1985, SCHAT 1982, ERNST 1983, ROZIJN 1984), this paper discusses the change of the $CaCO_3$-content during the past six decades and gives information on the variation of $CaCO_3$ and other mineral elements, pH, and organic matter content in the dune area of North Holland.

Due to the continuous eastward move of the island of Schiermonnikoog, a series of differently dated dune systems can be recognized (ISBARY 1936). Calcium carbonate measurements of these Schiermonnikoog dune systems were incorporated in this study to make a comparison possible with the North Holland dune analyses.

2. MATERIALS AND METHODS

Soil samples were collected in 1980 at Schiermonnikoog (53°29'N, 6°12'E) and in 1982, 1983 and 1984 in North Holland, in the dune area between Wijk aan Zee (mile post 51; 52°30'N, 5°21'E) and Camperduin (milepost 26;52°43'N, 4°40'E). These samples were at varying distances from the coastline but always in dune grassland vegetation with a predominance of *Festuca ovina* spp. *tenuifolia* (Sibth.) Čelak (nomenclature follows HEUKELS & VAN DER MEIJDEN 1983), the *Galio-Koelerion* in the southern, with *Koeleria cristata* (L.) Pers., *Festuca rubra* ssp. *arenaria* (Osb.) Richter and *Quercion robori petraea* with *Calluna vulgaris* (L.) Hull in the northern area. About a number of 200 sites were sampled along this North-South gradient and in transects from the coastline to the inner dunes of North Holland. In the latter case there is generally a more or less clear increase in the age of the dunes, the inner dunes originating from 1200–1300 AD or earlier periods (DOING & DOING-HUIS IN 'T VELD 1971). Besides this more or less large scale variation of the soil lime content, the variation of $CaCO_3$ and other soil factors with increasing soil depth was analysed. In 1984 also some soil samples were collected near Castricum in lysimeter 4, constructed in 1942 (STUYFZAND 1984).

At each sampling site, soil from different depths (0–10, 10–20, 20–30, 30–40 cm) was collected and dried overnight (80 °C) after removal of the vegetation layer. The location of the sites in North Holland, except the lysimeter location is indicated in *figs. 4* and *7*, with particular attention given to samples taken in the "Verbrande Pan" valley near milepost 34, BIJHOUWER's (1926) main study area.

For pH measurement, 10 grams of ovendried soil were extracted with 50 ml of distilled water (shaking for 2 h) and filtered before pH analysis. Another

5 grams were extracted with 100 ml 1 N HCl and, after shaking for 2 h and filtration, the extract was analysed for Ca, Mg, Fe and Mn using atomic emission (Na and K) or absorption (Ca, Mg, Fe, Mn) spectrophotometry on a Perkin Elmer 4000. The calcium carbonate content has been calculated using the HCl-extractable calcium analyses.

3. RESULTS

3.1. North-South transects

Along the large scale North-South transect from milepost 51 (Wijk aan Zee) to 26 (Camperduin) the superficial soil samples show an irregular decrease of the $CaCO_3$ content from high values in the southern part (up to 10% $CaCO_3$) to low values (less than 0.01% $CaCO_3$) in the northern part (*fig. 1*). In the area between mileposts 32 and 36 there is a steep change in the $CaCO_3$ content of the dune soil, particularly in the deeper soil layers (30–40 cm). Soil pH along the North-South transect closely follows the change in the $CaCO_3$ content (*fig. 2*). Fe, Mn, and Mg may have higher levels in the southern (Ca-rich) than in the northern part of the transect (*table 1*).

3.2. Seaward – landward transects

Coastline-inner dune transects (West-East gradient): there is no distinct relationship between the calcium content and the age of the coastal dunes (*table 1*, milepost 33), despite that there is a decrease in soil pH: alkaline or neutral conditions in the young coastal dunes (8.0–8.5) and acid conditions in the older inner dunes (4.3–4.5). Deeper soil layers may have a higher lime content, dependent on the

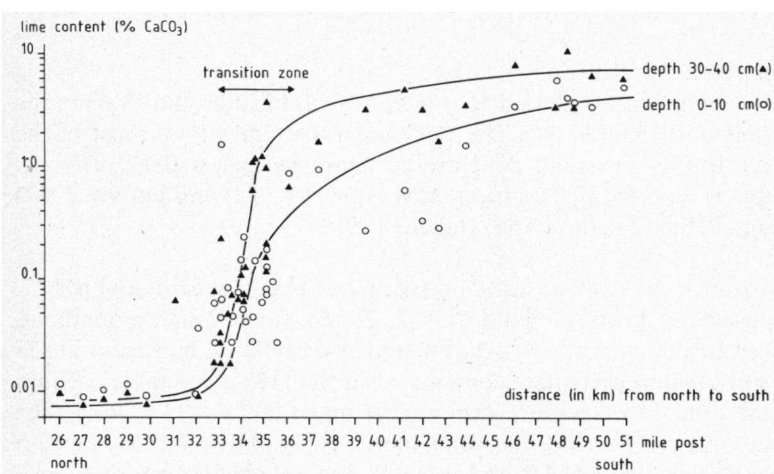


Fig. 1. Variation of the lime content (% $CaCO_3$) on dry weight basis of the dune soil) of dune soil samples taken along a North-South gradient in the dunes of North-Holland. The distance between two subsequent milepost numbers amounts to 1 km. Values of surface (0–10 cm) and deeper (30–40 cm) soil layers are represented.

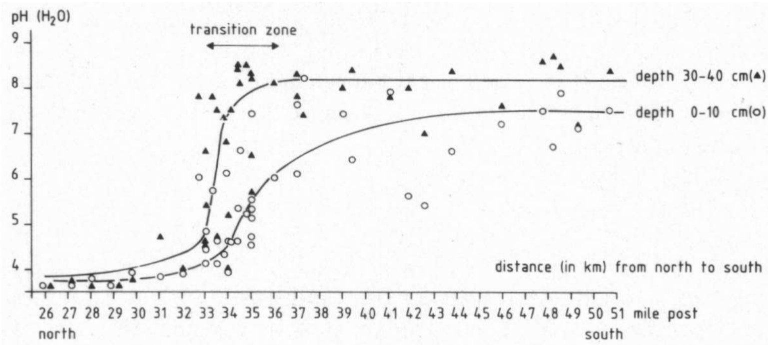


Fig. 2. Variation of the pH (H_2O) of dune soil samples along a North-South gradient from surface (0–10 cm) and deeper (30–40 cm) soil layers, see caption of fig. 1.

extent of carbonate leaching and on the $CaCO_3$ content of the original sand deposit. The soil samples taken near milepost 33 (33a, 33b, 33c) also show a landward decrease in Na^+ and Mg^{2+}, but not for Fe^{2+} or Mn^{2+}.

Coastline samples on the line of mileposts 37 and 39 contain far less $CaCO_3$ than do landward soil samples. The spatial heterogeneity of $CaCO_3$ content in this area (*fig. 4*), due to a complex history of deposition of differently-aged sand layers, hampers the determination of a clear-cut relationship between age and the lime content of the dune sand layers. Due to sand accretion by sea wind a more or less clear inversion of the calcium content can be seen at mileposts 35, 36 and 37: coastline samples containing more calcium in the upper than in the lower layers, samples from the inner dunes containing very little calcium in the upper layers compared with that of the lower layers (*table 2* and *fig. 4*).

3.3. "Verbrande Pan" area

The zone between mileposts 32 and 36 (*fig. 4, table 2*) includes the "Verbrande Pan" area (mileposts 33 and 34). The $CaCO_3$ content and pH of most of the samples taken in this particular zone are very low, i.e. below 0.03% (*fig. 1*). Higher values, as reported by HOFMANN & WESTHOFF (1951) and DOING (1964) were not found in the present samples, taken in 1982.

3.4. Relationship between $CaCO_3$ content of the soil and soil pH

Comparing both the North Holland (*figs. 1, 2* and *3*) and Schiermonnikoog (*fig. 6*) dunesystem data, it appears that there is a correlation between soil pH (H_2O) and soil calcium carbonate content, when the HCl-extractable calcium content of the dune soil is within certain (0.01 and 1.0% $CaCO_3$) limits. The correlation exists no longer beyond these limits: below 0.01% $CaCO_3$ the soil pH remains stable around 3.5–4.0, and above 1% the soil pH does not rise above 7.8–8.5 (*figs. 2* and *3*).

It appeared difficult to find a curve that fitted all data in *fig. 3*. For practical reasons the dotted lines were drawn to indicate the "bend" in the relationship

Table 1. Chemical analysis of dune soil samples taken between Bergen and Egmond along a North-South gradient (milepost 31, 33, 35) and of a seaward – landward gradient (mile post number 33 a, b, c); figures represent acid (1N HCl) and waterextractable ions.

Location			ion (ppm dry soil)							
Mile post number with distance from coastline (km)	sample number	depth (cm)	K	Na	Ca	$CaCO_3$%	Mg	Fe	Mn	pH (H_2O)
Waddendistrict North										
31	79	0–10	80/40	92/64	512/12	0.13	96/5	166/7	11.0/0	4.3
1,08 km landward		10–20	40/23	56/39	77/7	0.02	19/3	327/9	1.4/0	3.6
		20–30	39/23	53/51	162/9	0.04	35/4	256/8	2.8/0	3.5
		30–40	31/17	44/30	101/5	0.03	23/2	262/11	1.4/0	4.2
Dune district (South)										
35	90	0–10	53/22	19/7	4765/59	1.19	147/3	674/13	59.5/0.4	7.7
1,25 km landward		10–20	41/22	21/4	8782/45	2.20	95/0	398/0	33.0/2.3	8.5
		20–30	34/22	14/8	7563/57	1.89	79/2	340/0	14.6/0.3	8.5
		30–40	34/28	9/60	8043/61	2.01	70/1	376/0	12.5/0.3	8.4
Transition zone										
33a	201	0–10	28/22	14/1	2431/15	0.61	55/0	202/0	6.4/0.3	8.4
0,08 km landward		10–20	28/22	10/0	2486/15	0.62	51/0	173/0	6.4/2.3	8.0
		20–30	28/22	15/1	2366/17	0.59	54/0	202/0	6.4/2.3	8.2
		30–40	28/16	22/9	1966/13	0.49	40/1	209/0	6.4/0.3	8.5
33b	202	0–10	34/22	7/1	67/0	0.02	19/0	267/6	4.4/2.3	4.1
1,1 km landward		10–20	28/22	6/0	75/0	0.02	16/0	231/20	10.5/2.3	4.3
		20–30	28/22	0/0	91/0	0.02	18/0	194/6	14.6/6.4	4.5
		30–40	28/28	6/0	97/0	0.02	24/0	253/0	16.6/2.3	4.6
33c	203	0–10	47/28	13/9	191/0	0.05	22/0	267/42	4.4/4.4	4.4
2,0 km landward		10–20	34/22	3/0	77/0	0.02	13/0	332/27	4.4/2.3	4.3
		20–30	28/22	2/0	95/0	0.02	16/0	296/35	8.4/2.3	4.5
		30–40	28/22	15/0	123/0	0.03	21/0	332/27	10.5/2.3	4.5

Table 2. Comparison of the $CaCO_3$-content (% dry soil) of dune soil reported by BIJHOUWER (1926) and results in the present paper, sample numbers refer to locations, indicated in *fig. 4*.

milepost number	sample number	Bijhouwer	Rozema et al. this paper
		0–30 cm	0–10 cm – 30–40 cm
31	78	0.075 –0.4	0.12 – 0.15
	79	0.05 – 0.075	0.13 – 0.03
	80	0 – 0.05	0.65 – 0.07
32	82	0.075– 0.4	0.03 – 0.03
	83	0.05 – 0.075	0.01 – 0.01
	84	0.075– 0.4	0.04 – 0.01
	2	0 – 0.05	0.03 – x
	25	0 – 0.05	0.067– 0.087
33	202	1.0 – 2.0	0.02 – 0.02
	203	0.05 – 0.4	0.05 – 0.03
	204	1.0 – 2.0	1.74 – 0.26
	24	0.075– 0.4	0.071– 0.038
	23	0.05 – 0.075	0.094– 0.055
	207	0.05 – 0.075	0.03 – 0.02
	22	0 – 0.075	0.050– 0.78
	21	0 – 0.05	0.081– 0.076
	4*	0 – 0.075	0.16 – 0.12
	15	0.4 – 1.0	0.24 – 0.07
34	85	0.4 – 1.0	0.40 – 0.17
	27	1.0 – 2.0	0.02 – 0.02
	87*	0.4 – 2.0	0.06 – 0.07
	20	0.05 – 0.075	0.046– 0.142
	88*	2.0 – 3.0	0.26 – 0.08
	50	1.0 – 2.0	0.05 – 0.02
	211**	0.4 – 1.0	0.05 – 1.21
	206**	0.4 – 1.0	0.03 – 0.69
	19	0.4 – 1.0	0.16 – 1.30
	18	1.0 – 2.0	0.07 – 1.36
35	90	1.0 – 2.0	1.19 – 2.01
	91***	1.0 – 2.0	0.14 – 0.23
	16	0.4 – 2.0	0.08 – 0.13
	17	1.0 – 2.0	0.09 – 1.09
	92***	1.0 – 2.0	0.20 – 0.17
	93***	3.0 – 4.5	0.14 – 4.00
	14	1.0 – 2.0	0.27 – 0.19
	89	1.0 – 2.0	0.35 – 0.22
	14	0.4 – 1.0	0.10 – x
	8	0.4 – 1.0	0.03 – x
26	94	1.0 – 2.0	0.79 – 0.19
	95	3.0 – 4.5	0.75 – 0.10
	96	4.5 – 6.0	0.21 – 0.74
37	97	2.0 – 3.0	1.10 – 0.29
	98	3.0 – 4.5	0.48 – 1.42
	13	6.0 –15.0	6.89 –11.21
	12	4.5 – 6.0	1.02 – 1.84

* sites in the "Verbrande Pan"
** sites in the "Bokkenweide"
*** sites in the "Heerenweide"
x not determined

between soil calcium carbonate and soil pH, around 0.3% $CaCO_3$. Almost the same relationship has been described by BOERBOOM (1963). However, the location of this "bend" is far less precisely 0.3% $CaCO_3$, but in fact somewhere between 0.1% and 0.5% $CaCO_3$. The curve that is drawn in *fig. 3* was calculated for data with a soil pH less than 8. The equation and correlation coefficient appear in the upper part of the graphs.

The values of these correlation coefficients increase with greater depth. It seems that this tendency is not dependent on the calcium carbonate content in surface or deeper layers (*fig. 3*).

3.5. Comparison of the lime content in the dune soil in 1923 and 1983

The Ca-content of 46 of all the samples collected in 1982 could be compared with $CaCO_3$-measurements made in 1923 by BIJHOUWER (1926), using a map of the dune area between mileposts 31 and 38 in Bijhouwer's thesis (*fig. 4*).

Before interpretating of *fig. 4* and *table 2*, two points must be considered.

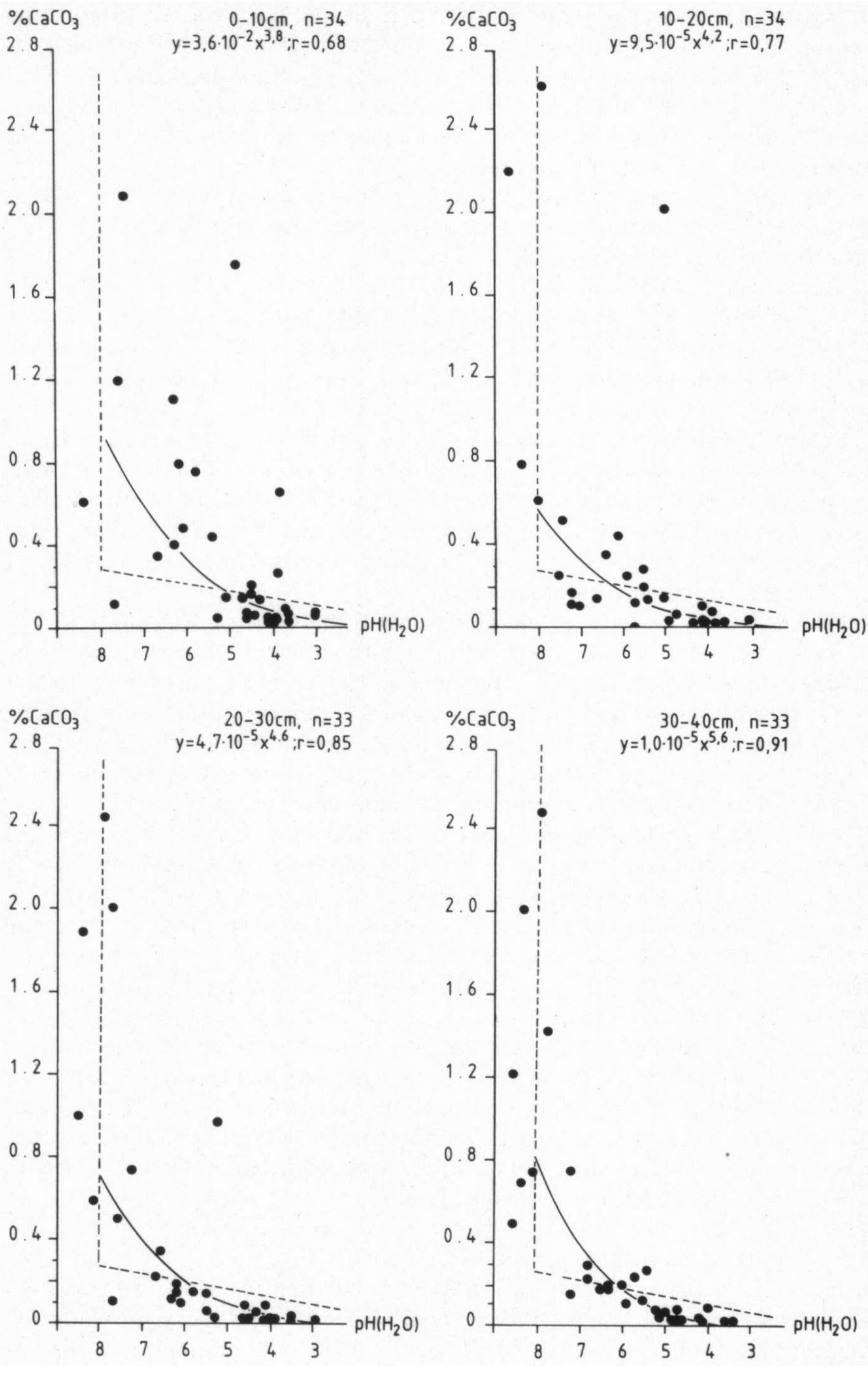
1. BIJHOUWER (1926) mixed soil collected from 0–30 cm. This has no consequences in soil profiles with $CaCO_3$ completely leached out or in profiles with no leaching at all, but in soils with a decrease of $CaCO_3$ in the surface layers relative to the deeper layers Bijhouwer's measurements give a weighed average of upper and lower layers.
2. The calcium carbonate of the dune sand as mapped by BIJHOUWER (1926) in *fig. 4* is presented as *ranges* (*table 2*) with an upper and lower limit. The upper limit (high % $CaCO_3$) may refer to $CaCO_3$ in deeper soil layers and the lower limit to surface soil layers, and a comparison was made with the measurements in the 30–40 cm layer of the present study (closed circles in *fig. 5*; open circles refer to a comparison of the 0–10 cm values with the lower limit of each of Bijhouwer's ranges of calcium carbonate content).

With some exceptions in the range of low $CaCO_3$ values ($<$ 0.2% $CaCO_3$) all points are plotted above the $Y = X$ line, representing a fall in the $CaCO_3$ content in the course of the 60 years between 1923 and 1982 (*fig. 5*).

In *fig. 5* the lines drawn indicate the possible dependence of $CaCO_3$ leaching on the original $CaCO_3$ content. (i). At low $CaCO_3$ values (0–0.1%) a decrease can hardly be detected partly for methodological reasons (cf. *fig. 6*) and partly due to the presence of calcium ions on the ion exchange sites, developed with the increase of the organic matter content; (ii), in the range between 0.1 and 1.0% $CaCO_3$ the rate of decalcification is high, and this process seems to be slower with higher values of the lime content. This may be due to the presence of larger shell fragments, causing incomplete contact with percolating rainwater. Leaching in the surface soil layers will be more rapid than in the deeper layers when there is development of organic matter.

3.6. Decalcification in Schiermonnikoog dunes

As the island of Schiermonnikoog is moving eastward by developing dune ridges along that part of the island, the age of the dune systems increases from east to west (*fig. 6*) cf. ISBARY, (1936), ROZEMA (1978). The original lime content


%CaCO3
0-10cm, n=34
y=3,6·10-2x3,8;r=0,68
10-20cm, n=34
y=9,5·10-5x4,2;r=0,77
20-30cm, n=33
y=4,7·10-5x4,6;r=0,85
30-40cm, n=33
y=1,0·10-5x5,6;r=0,91
pH(H2O)
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0
8
7
6
5
4
3

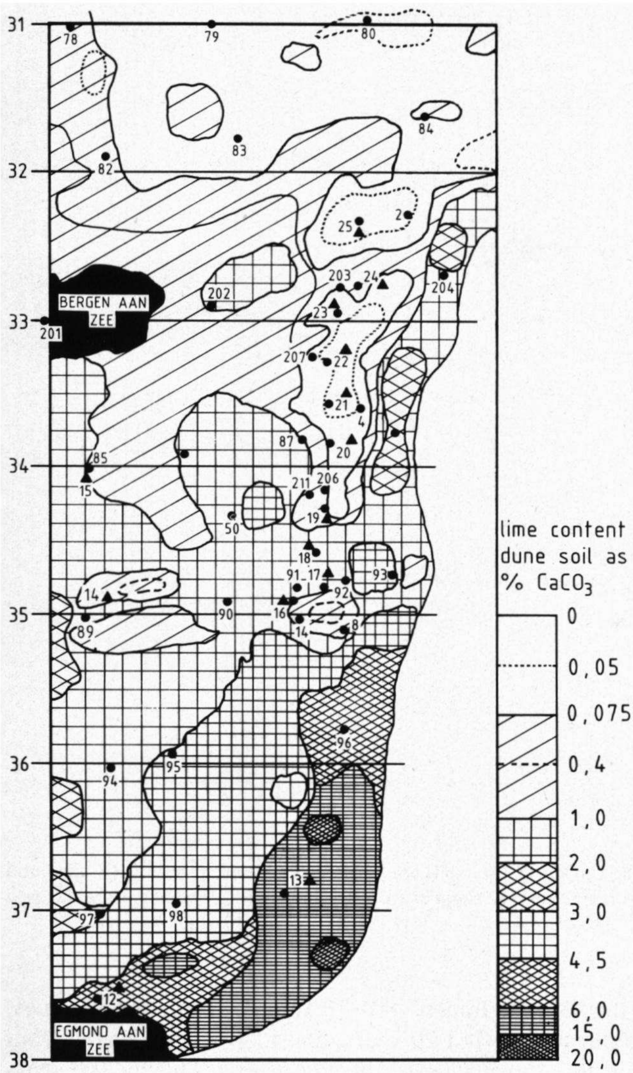


Fig. 4. Variation of the lime content (% $CaCO_3$) in the dune area between Bergen aan Zee and Egmond aan Zee in 1923/1924 (after BIJHOUWER 1926). Numbers in the map indicate the location of sampling sites of the present paper (see also table 2 and fig. 8 for a comparison of the change in lime content of sites from 1923/1924–1983).

◀ Fig. 3. Relationship of soil pH and $CaCO_3$ content (% dry soil) with different soil depths (0–10, 10–20, 20–30 and 30–40 cm). Based on 33 soil samples in the lime transition zone between milepost 31 (2 km North of Bergen aan Zee) and milepost 39 (1 km South of Egmond aan Zee).

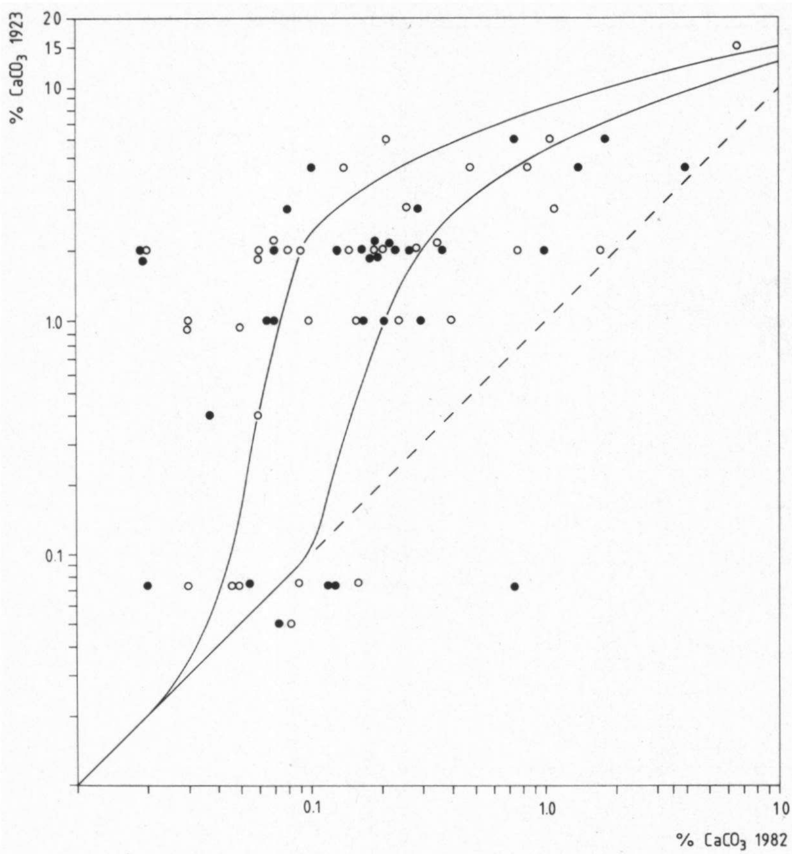


Fig. 5. Scatter diagram of the $CaCO_3$ (% dry soil) content of sites sampled in 1923 (Y-axis) and in 1982 (X-axis). Open circles represent 1982 samples from the surface (0–10 cm) layers and closed circles samples from deeper (30–40 cm) layers.

of the youngest dunes, the "Kobbeduinen" (10–15 and 15–20 cm depth values) shows a rapid decrease during the first 20 years, considering the decline from 0.75% to 0.5% $CaCO_3$ in the upper 5 cm of the soil profile. During 100 years of leaching and further dune soil development the $CaCO_3$ content drops to 0.125% $CaCO_3$ or lower, 0.065% in the surface layers, with no measurable further decrease in the oldest dune system, "Kooiduinen". Thus, during the first 120 years of dune soil development, a drop from 0.75 to 0.065% $CaCO_3$ (on dry weight basis of the dune soil) may occur.

In the deeper soil layers (10–15, 15–20 cm) with higher pH-values and a low organic matter content the decalcification of the soil is not directly promoted by the process of humus-development (the thickest layer with organic matter in the sampled sites was 3 cm), and seems to take place more slowly, with a decalcification rate of 0.25% $CaCO_3$ per 100 year.

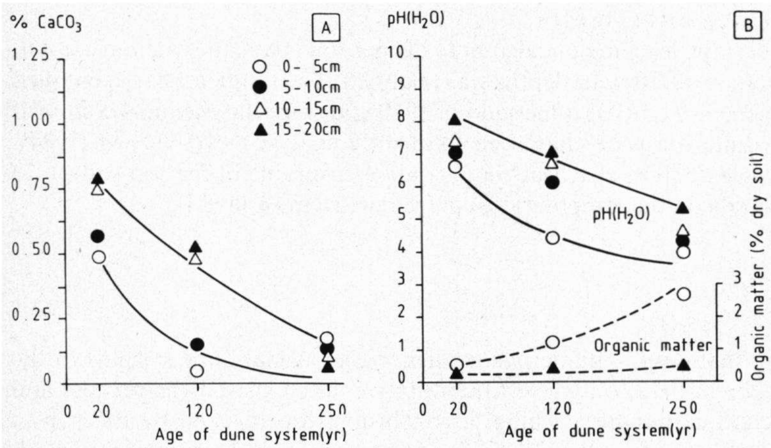


Fig. 6. (A) $CaCO_3$ content (% dry soil) of three dune systems with increasing age on Schiermonnikoog (Strandvlakte, Kobbeduinen, Kooiduinen).
(B) Change in pH (H_2O) and organic matter (loss on ignition at 550 °C). Samples collected in 1980 in open vegetation with *Ammophila arenaria* and *Festuca rubra* ssp. *arenaria*. See also ROZEMA (1978).

Fig 6 again indicates that in the $CaCO_3$ content range below 0.2% it becomes difficult to detect a further decrease in the lime content.

Table 3. Calcium and calcium carbonate content of soil samples taken at lysimeter 1 near Castricum at different depths (cm), content of calcium as percentage or ppm of the dry soil acid (1 N HCl) and waterextractable.

sample number	depth (cm)	Ca acid extractable %	Ca water extractable ppm	$CaCO_3$%	pH (H_2O)
1	0–10	1.7	248	4.2	7.1
bare	10–20	2.3	370	5.7	7.2
sand	20–30	2.2	417	5.5	7.3
	30–40	2.2	498	5.6	7.3
	40–50	2.1	422	5.2	
2	0–10	2.0	276	4.9	7.3
bare	10–20	2.2	391	5.5	7.9
sand	20–30	2.1	505	5.3	7.4
	30–40	2.3	486	6.5	7.3
	40–50	2.6	441	6.6	
3	0–10	1.1	59	2.8	7.3
bare	10–20	1.9	309	4.9	7.4
surface	20–30	1.9	378	4.7	7.4
covered with moss	30–40	1.9	511	5.0	7.4
layer	40–50	2.0	518	5.1	

3.7. Lysimeter soil samples

In order to test the leaching of calcium to deeper soil layers the calcium content of samples taken at different depths was analysed. The lysimeter has been filled with homogeneously mixed dune sand in 1942 and since the chemical composition of the dune soil water has been frequently analyzed (STUYFZAND 1984). The data (*table 3*) show that leaching is only measurable in the top soil (0–10 cm), particularly on the sampling site covered with a moss layer.

4. DISCUSSION

4.1. General results

It is striking that despite numerous studies in the coastal dune systems of the world (RANWELL 1972) only a few quantitative data exist on the process and rate of calcium carbonate leaching, a conclusion also reached by BAKKER et al. (1979). Analysis of sand dune soil samples collected along a North-South gradient showed a steep change in the soil calcium carbonate content (2%–0.01%) in the dune area between milepost 36 and 32 possibly due to differences in deposition of shell fragments recently and in the past. Moreover the "Verbrande Pan" area, located between milepost 34 and 33 (*figs. 4* and *7*) shows a coast-landward gradient in the calcium carbonate content related to the age of the dune formation. A decrease in soil pH (H_2O) was observed parallel to the calcium carbonate transition (*figs. 1, 2*).

The calcium carbonate content of surface layers in the dune may be influenced by (i). deposition of new sand, containing shell fragments, (ii). cycling of minerals, amongst which calcium ions, between soil and vegetation, (iii). several kinds of disturbance (digging by rabbits, wind erosion, possibly enhanced by trampling, excavations by man for various aims: e.g. road development, agriculture, watercatchment, coastal defence etc., see STEENKAMP et al. 1981).

SALISBURY (1952) reported a change from 4% $CaCO_3$ (pH 8.2) to 0.2% (pH 6.4) for the South Port dunes (Great Britain), and from 0.42% (pH 7.2) to 0.05% (pH 6.3) in the dune system of Blakeney Point (Great Britain), over a 200 year period. In the present study a decrease from 0.75% to 0.125% $CaCO_3$ for deep layers; and from 0.5 to 0.06% $CaCO_3$ respectively for surface layers is found, in dunes with *Festuca rubra* ssp *arenaria* vegetation on the island of Schiermonnikoog over a 230 year period, which thus resembles the above decline in the Blakeney Point data. In the Schiermonnikoog data the pH drop in the surface layers was from 0.7 to 4.0 and for soils taken from 15–20 cm depth from 8.0 to 5.2. RANWELL (1972) reported a decrease from 5% $CaCO_3$ to 0% in the 0–10 cm surface layer within 300–400 years in several British dune systems.

As was shown in *fig. 6*, organic matter may also increase with the age of dune systems cf. ROZEMA et al. 1977. In coastal dunes on Schiermonnikoog with a sparse *Festuca rubra* ssp *arenaria* vegetation, the organic matter content increased to 3% of the soil dry weight after 250 years of dune soil development (*fig. 6*).

Figs. 2, 3 and *6* showed that calcium carbonate leaching from 10% to about 1% is not accompanied by a decrease in the soil pH. Apparently, the potentially acidifying action of CO_2 dissolving in the soil moisture is buffered in this range of the dune soil calcium carbonate content.

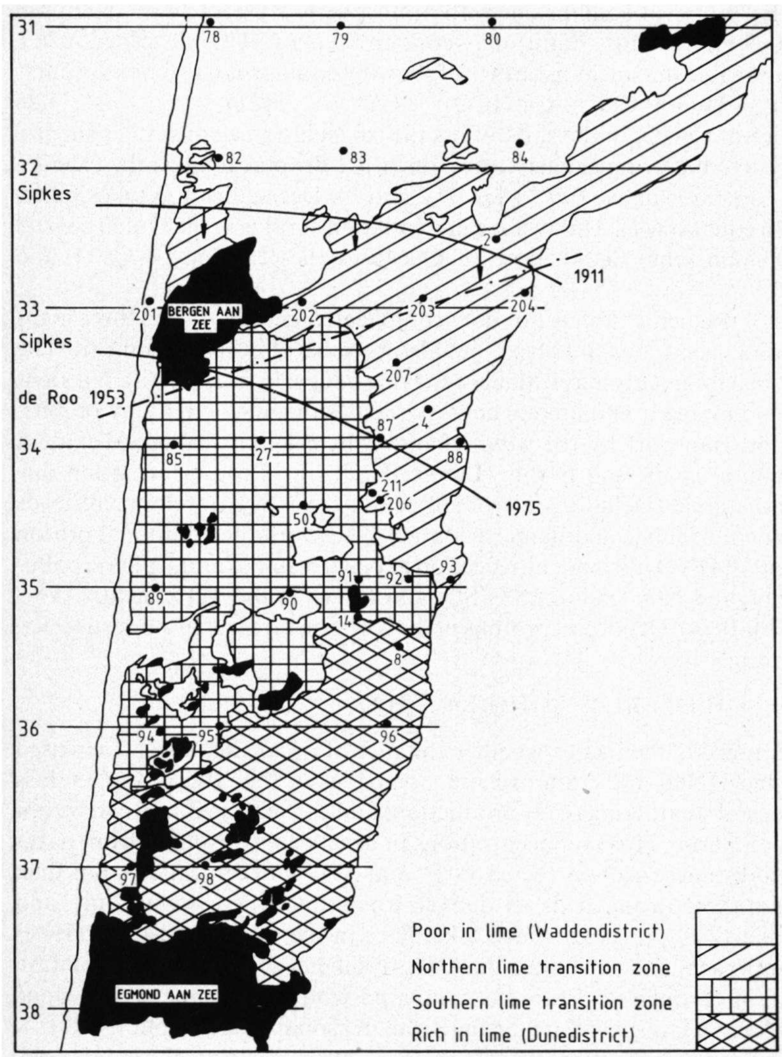


Fig. 7. Location of lime transition zones according to DOING (1964), based on classification of vegetation types, with the lime "border" and changes in it according to DE ROO (1953) and SIPKES (1975). Numbers refer to samples in table 2. Number 4, 87 and 88 are in the "Verbrande Pan" valley, 206 and 211 in the "Bokkenweide" and 91, 92 and 93 in the "Heerenweide".

4.2. Decalcification

Decalcification as a result of $CaCO_3$ dissolving in the soil moisture is a process involving three components i.e. the solid $CaCO_3$, the atmospheric gaseous phase with amongst others CO_2, and the soil moisture with dissolved Ca^{2+}, CO_3^{2-}, H^+, HCO_3^-, H_2CO_3 and CO_2. (APPELO 1982a, 1982b).

The solubility of calcium carbonate in pure water is low; the solubility product is 5.10^{-9} $mol^2.1^{-2}$. With dissolved CO_2, the solubility of $CaCO_3$ in water increases significantly. Water in equilibrium with atmospheric CO_2 (pCO_2 = 300 ppm v/v = 0.0003 atm. = $10^{-3.5}$ atm) may contain 90 mg $CaCO_3$ dissolved in 1 l. In this solution (i.c. the soil moisture) the following equilibrium reactions occurs:

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2 \gtrless Ca^{++} + 2HCO_3^- \quad (1)$$

The presence of $CaCO_3$ in the soil buffers the soil sulution against pH changes. Apparently this buffering capacity prevents a pH drop as long as the calcium carbonate content is above 0.3% (*figs. 1, 2* and *3*). Decalcification takes place, maily due to equation (1). The average precipitation surplus in the Dutch coastal region (200 mm/year, BEUKEBOOM 1976) causes the leaching of Ca^{++} and HCO_3^-.

Analysis of decalcification is not only complicated because of the three components (solid, gas, water) involved, but also because of other reasons: (i). The size of the shell fragments may influence the rate of decalcification. (ii). Nutrient cycling including plant and animal activity such as digging activity by rabbits, but also sand transport by the wind, changes the calcium carbonate content and distribution in the soil profile (ERNST 1985). (iii). Proton formation due to plant and animal (including microbial) activity (iv). Soil development leads to development of fulvic and humic acids. (v). There may be additional proton development of HNO_3 through nitrification and as a result of atmospheric pollution with SO_2 and NO_x leading to H_2SO_4 and HNO_3 in the soil moisture (VAN BREEMEN et al 1984). Of course, protons in the soil moisture will promote decalcification through

$$CaCO_3 + H_3O^+ \rightarrow Ca^{2+} + HCO_3^- + H_2O$$

The question arises then as to whether the rate of decalcification is increased by H_2SO_4 and HNO_3 in the atmosphere. Some idea of the ratio of $CaCO_3$ loss through natural weathering (CO_2-production) and through acid rain can be obtained by comparing HCO_3-concentrations in drainwater (resulting from natural weathering) and seasalt-corrected SO_4^{2-} and NO_3^--concentrations. It is then assumed that these strong acids are derived from atmospheric inputs only, and are not affected by processes which take place in the soil. STUYFZAND (1984) used this approach, and calculated that 33% (lysimeter 1) of $CaCO_3$ dissolution on bare soil is through acid rain, as compared with 44% lysimeter 4 in dune soil with *Pinus nigra* growth. Starting from reasonable assumptions, KLIJN (1981) calculated a decalcification rate of 45 g $CaCO_3$/1340 g soil per 100 year. This equals a decrease of 0.034% $CaCO_3$ of the dry weight of the soil per year. The time course of decalcification observed in the Schiermonnikoog dunes (*fig. 6*) closely resembles the data presented by SALISBURY (1952) and OLSON (1958).

The content of calcium carbonate seems to decrease exponentially with time. This has been interpreted as the result of increasingly incomplete contact of the percolating water with larger shell fragments, that remain when decalcification proceeds (KLIJN 1981). In this case the time course of decalcification can be described by

$$C_t = C_o.e^{-\lambda t}$$

where C_o = the primary $CaCO_3$ content in the dune sand
C_t = the $CaCO_3$ content after t years
λ = constant of decalcification

Using such a negative exponential, STUYFZAND (1984) presented a decalcification constant of 6.7×10^{-4} year $^{-1}$ for lysimeter data of North Holland sand dunes near Castricum (52°33'N, 4°.40'E). The Schiermonnikoog data (*fig. 6*) with C_o = 0.75% $CaCO_3$ and C_{230} = 0.125% $CaCO_3$ (10–20 cm depth) give a decalcification constant of 7.7×10^{-3} year^{-1}, and the data for 0–10 cm depth give a decalcification constant of 6×10^{-3} year^{-1}. An important difference between the Schiermonnikoog and Castricum dune site is the different primary content of $CaCO_3$ of the dune sand, less than 1% for the former and between 5–10% in the latter. Nevertheless there is no difference in the decalcification rate since the values of the decalcification constant are in the same order of magnitude.

With regard to the calcium carbonate transition zone discussed in this paper important questions can be posed:

i. Has this lime transition zone moved southward?
ii. Has the recent tendency of increasingly acid precipitation increased the decalcification rate?
iii. Has the extension of the area, poor in calcium carbonate, been followed by vegetation changes?

Analysis of the calcium content of soil samples taken at the lysimeter near Castricum (*table 3*) (see STUYFZAND 1984) might allow calculation of the decalcification constant with:

C_o = the calcium carbonate content of the deepest soil samples taken (40–50 cm), which probably equal the primary content of calcium carbonate of the dune sand.
C_t = the content of $CaCO_3$ in the surface soil layer (0–10 cm) in 1984
t = 43 years

For samples 1 and 2 (without vegetation) and 3 (with moss cover) the values for the decalcification constant are 5.0×10^{-3} year^{-1}; 4.7×10^{-3} year^{-1}; 13.9×10^{-3} year^{-1} respectively. With these rates of decalcification the calcium carbonate leaching from 3.5% to 0.3% in the upper 10 cm of the soil profile would take 491; 523 and 176 years for soil samples 1, 2 and 3 respectively. These calculations indicate 7–20 times faster decalcification rates than those made by KLIJN (1981) and STUYFZAND (1984). Obviously, the outcome of these calculations strongly depends on the volume of the soil layers that are considered. The longer period in STUYFZAND's calculation of leaching (3670 years), necessary for a

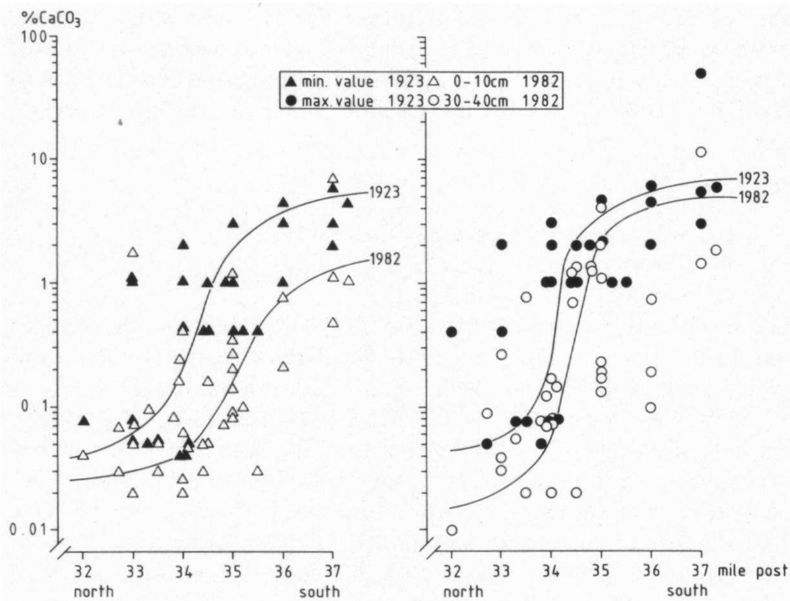


Fig. 8. Comparison of variation of the $CaCO_3$ content (% dry soil) in the transition area between milepost 32 (North) and 37 (South) based on BIJHOUWER's data (1923) and results of the present paper (1982). (see also figs. 4 and 5).

$CaCO_3$ decrease (3.5% $CaCO_3$ to 0.3%) than calculated in this paper (176–523 years) is because STUYFZAND's calculations refer to calcium carbonate leaching of *all* the dune sand present in the lysimeter. KLIJN (1981) calculated decalcification rates expressed as the increase in dm of the (totally) decalcified part of the soil profile per century for soils with a primary $CaCO_3$ content higher than 1%. For this reason the decalcification rates in this paper cannot be compared to KLIJN's (1981) data.

From the decalcification rate calculated in this paper, we conclude that:

i. differences in decalcification rates calculated for surface layers may exist on adjacent sites due to differences in vegetation cover (*table 3*).
ii. decalcification rates calculated for surface layers (0–10 cm) of the Schiermonnikoog dunes (6–7.7 × 10^{-3} year^{-1}) are of the same order of magnitude compared to calculations made for the decrease measured in the calcium carbonate content in a North Holland Dune reserve lysimeter (4.7 × 10^{-3} – 13.9 × 10^{-3} year^{-1}).

Below a certain limit of $CaCO_3$ (the "bend" indicated in *fig. 3* around 0.3% $CaCO_3$) the buffering capacity of the dune soil is apparently reduced and the carbonate decrease runs parallel to increased acidity (*figs. 2, 3* and *6B*).

4.3. Calcium carbonate, decalcification and dune vegetation

The spatial variation of the soil carbonate content in the "Verbrande Pan" area is presented in *fig. 4*, and a comparison was made between BIJHOUWER's (1926) recordings and the present data from 1982 in *fig. 5* and *table 2*. Nearly all sampled sites showed a decrease in the lime content during the 1923–1982 time-span. The question can therefore be raised whether the lime border ("kalkgrens") between the phytogeographical Wadden- and Dunedistricts moves southward as a result of decalcification (*cf.* DE ROO 1953, DOING 1964, p. 30, SIPKES 1975, SCHENDELAAR 1978 (see *fig. 7*)).

The dune area north of milepost 32 contained less than 0.075% $CaCO_3$, the area between mileposts 29 and 30 less than 0.05% $CaCO_3$ (*fig. 4*) and could therefore be characterized as typically northern Wadden district (*fig. 7*). In the southern area, richer in lime (more than 0.075% $CaCO_3$) the "Verbrande Pan" and "Bokkenweide" at milepost 34 (*figs. 5, 7* and *table 2*) have a lime content less than 0.075%. The "Heerenweide" at milepost 35 (*fig. 7* and *table 2*), that has been earlier reported as relatively rich in lime, according to DOING (1964) and BIJHOUWER (1926) (1% < $CaCO_3$ content of the dune soil < 2%) now has a far lower carbonate content (less than 0.1% $CaCO_3$), as we found in the present study.

The dune soil analyses reported in the present study make clear that the area with a carbonate content less than 1% has extended from milepost 34 in 1923 to milepost 36 or 37, using both surface (0–10 cm) and deeper (30–40 cm) layers as a starting point. This is clearly illustrated by the shift of the lime transition curves drawn in *fig. 8*. Detailed analysis of vegetation changes in 22 permanent quadrats located in between mileposts 31 and 38 this particular area have been made over the past 33 years (1950–1983) (PHILIPPENS, 1984). They have revealed some very interesting trends in relation to the decalcification (rates) reported in this paper.

Firstly, PHILIPPENS demonstrated not only a significant decline in the number of superficially rooting calcicolous plant species, but also an increase in the number of calcifuge species. based on the classification system by ELLENBERG (1978). Secondly, PHILIPPENS provides evidence that the lowering of the ground water-table in the period 1950–1970 is not directly related to the observed vegetation changes.

In this paper the rate of calcium carbonate leaching in North-Holland coastal dunes was reported and discussed in comparison with dune systems on Schiermonnikoog (cf. ISBARY 1936). In the 250 year old dune system "Kooiduinen" the pH of surface and deeper (20 cm) soil layers, was 3.6–4.5 in all dune vegetation types ranging from sparsely vegetated *Festuca rubra* ssp. *arenaria* sites to dune forests (with *Betula pubescens* and *Quercus robur*). The dune area in North-Holland with a dune soil calcium carbonate content up to 1% extended about two kilometers southwards during the past 60 years. The increased acidity of rain water, such as reported by VERMEULEN (1977) for the province of North-Holland could accelerate the 'natural' decalcification rate of the dune soil. Variation in the decrease of $CaCO_3$ at adjacent surface sites however may mask the evidence for increased decalcification rates due to acid precipitation. On the other hand calculations made by STUYFZAND (1984) indicate that acid rain may significantly increase the decalcification rate on soils with or without a vegetation cover. In both the coastal dunes of North-Holland and the dunes of Schiermonnikoog high levels of salt spray can be measured (containing 50 mmol/l Mg^{++} and 10 mmol/l Ca^{++}, ROZEMA et al. 1982; ROZEMA et al. 1983). However, the buffering capacity will be low due to the relatively low bicarbonate content of the salt spray. The observation of absence of acid rainborne damage in coastal dune forests and woodlands can therefore not simply be related to high levels of salt spray. The interrelations of decalcification, acid rain salt spray and dune vegetation deserve further investigation.

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