

ACIDITY AND CHEMICAL CHARACTERISTICS OF DIRECT PRECIPITATION UNDER  
FOREST COVER IN THE WINTER-PHENOPHASE

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Abstract

From november 1983 to march 1984 samples of direct rainfall were collected at 5 locations and for a total of 12 different situations ( urban zone, free field, under forest canopy ) in East-Flanders/Belgium. The over-all mean pH-values of rainwater collected under a forest canopy are lower than in the adjacent free field. The highest pH-values are measured in urban zones. The lowest pH-values are found under beech and scots pine, whereas pH under ash, alder, oak and in the free field are greatly comparable. Important variations in time, following the same pattern in all cases, exist, proving the importance of external influences. The chemical analyses of the rainwater also indicates important variations and differences. The highest concentration of  $SO_4$ , Na, K, Ca and Mg is found in water collected under forest canopy. Maximal values are typical for stands of scots pine. More research is needed to explain this phenomenon.

PLAN

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Some characteristics of rainwater, resulting from direct precipitation, were studied in 3 forest areas ( Gontrode, Wachtebeke, Buggenhout ) and 2 urban zones ( Ghent, Zelzate ) all situated in E. Flanders/Belgium and within a maximal distance ( Zelzate-Buggenhout ) of 35 km of each other.

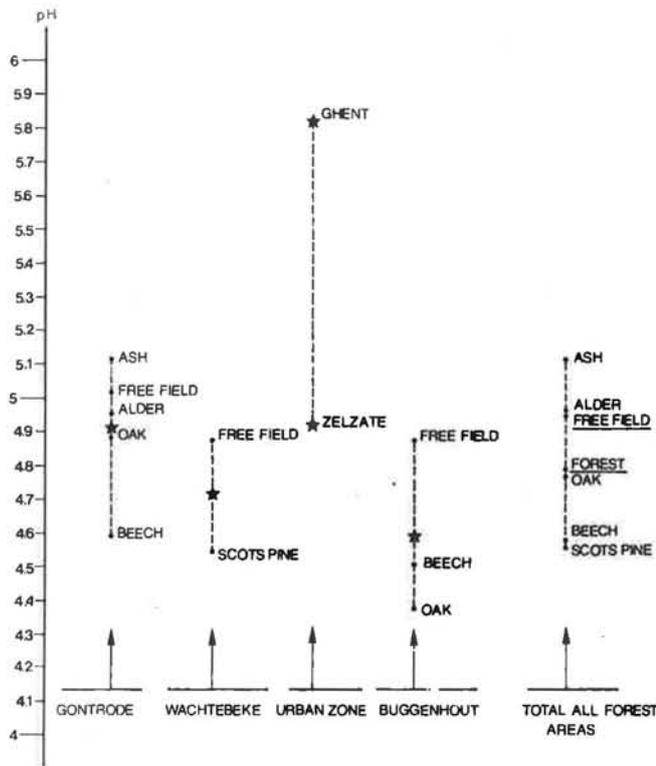
A total of 12 measuring-points were spread over the 5 locations, some situated under a forest canopy and others in the free field. At each point a first series of 8 recipients was set up to collect direct precipitation.

The content of the recipients was analyzed every 2 weeks over a period of 5 months, producing a total of 9 time-samplings ( systematic analysis =  $12 \times 8 \times 9 = 864$  recipients analyzed ).

At 7 measuring-points a second or parallel series with 8 recipients each was set up ( 5 at Gontrode; 2 at Wachtebeke ) as near as possible to the measuring-points, belonging to the systematic network at the same location. The direct precipitation-water, collected at these points, was analyzed within 24 hours after rainfall started, provided rain fell after a dry period of at least 3 days ( parallel analysis =  $8 \times 8 \times 16 = 896$  recipients analyzed ).

1. The acidity of rainwater

Suitable globalization and grouping of measurements indicate that the over-all mean pH-value of direct precipitation-water attains 4.88, but also that significant differences in pH-value exist ( Tab. 1 ) according to :



- The sampling method ( systematic or parallel analysis ).
- The general characteristics of locations ( forest; free field; urban site ).
- The dispersion in space ( 5 geographic locations ; 3 forest locations ), even at a fairly short distance.
- The differences in forest cover
  - a. between hardwoods and conifers ;
  - b. between different hardwood-covers.
- The dispersion in time of measurements ( time function ).

The variability of the acidity of rainwater precipitation, is a basic factor to be reckoned with ( Fig. 1 ).

Fig. 1 : Mean pH-values for the whole observation period (\* : Mean value for location ).

### 1.1. The sampling method

For the totality of all measurements, for all measurements in the free field and for all measurements at Wachtebeke, mean pH-values, obtained by parallel analysis, are significantly higher as those obtained by systematic analysis ( Tab. 2 ).

However, as no significant differences exist in most cases and as eventual significant differences are rather restricted, systematic analysis seems recommendable as a method.

### 1.2. Spatial variation

Mean pH-values for the whole observation period and without considering local ecological situations, are subject to variations in space.

Tab.1 : Mean pH for globalized and regrouped measurements.

Total 4.88	Sampling method	Parallel an.	: 4.90		
		Systematic an.	: 4.85		
	Location	Ghent	: 5.82		
		Zelzate	: 4.91		
		Gontrode	: 4.91		
		Wachtebeke	: 4.71		
		Buggenhout	: 4.59		
	Month	November	: 4.39		
		December	: 4.99		
		January	: 5.02		
		February	: 4.52		
		March	: 4.93		
	Situation	Free field 4.94	Gontrode	: 5.01	
			Wachtebeke	: 4.88	
			Buggenhout	: 4.88	
		Urban site 5.38	Ghent	: 5.82	
			Zelzate	: 4.91	
		Forest 4.78	Conifers	: 4.54	
			Hardwoods	: 4.82	Oak : 4.76
					Beech : 4.57
		Gontrode	: 4.88	Ash : 5.11	
				Alder : 4.96	
				Oak : 4.88	
				Beech : 4.60	
		Buggenhout	: 4.41	Beech : 4.51	
				Oak : 4.38	

Mean pH reaches an over-all maximum of 5.82 at Ghent and a minimum of 4.59 at Buggenhout.

Although the high  $\chi^2$ -value ( = 56.29 ), obtained through the Bartlett-test prevents a total variance-analysis, a comparison by pairs nevertheless indicates that most bilateral differences are significant ( Tab. 3 ). More research is required to understand and interpret the differences between the situation in the urban zone of Ghent, thought to be highly polluted, and the situation under a forest cover of oak or beech at Buggenhout.

Tab.2 : t-test on differences in mean pH-value, obtained by systematic parallel analysis.

Universa	Systematic analysis	Parallel	t-value	Degrees of liberty
Global	4.80942	4.9028	2.03399*	1351
Free Field	4.79526	5.06221	3.7151***	389
Forest	4.81504	4.83685	.382461	960
Gontrode Total	4.91632	4.91038	.108652	1028
Free field	4.8889	5.07775	1.95741*	227
Forest	4.92334	4.85923	1.01179	799
Oak	4.81854	4.91531	.887375	227
Beech	4.66805	4.53649	1.00910	191
Ash	5.18195	5.06009	.863865	192
Alder	5.03581	4.90505	1.12001	183
Wachtebeke Total	4.51905	4.8756	4.21795***	321
Free field	4.34662	4.7131	3.08734**	160
Scots pine	4.69149	5.03625	3.00266**	159

Tab.3 : t-values for comparison in pairs of mean values pro location ( cfr. Tab. 1 ) over the whole observation period ( df = degrees of freedom ).

	Gontrode	Zelzate	Wachtebeke	Buggenhout
Ghent	9.0595*** df = 1108	6.9641*** df = 152	10.4904*** df = 401	13.1909*** df = 294
	Gontrode	0.0066 df = 1102	3.7166*** df = 1351	5.3313*** df = 1244
		Zelzate	1.9919* df = 395	4.0506*** df = 288
			Wachtebeke	1.9405 df = 537

### 1.3. Influence of the forest canopy

Precipitation-water is less acid in the free field in comparison to the situation under a forest canopy ( Tab. 1 ). t-tests indicate highly significant differences for a global approach forest/free field, as well as for Wachtebeke and Buggenhout separately, but not for Gontrode.

Forest cover/Free field	Gontrode	t = 1.9571	df = 1029
	Wachtebeke	3.7617***	321
	Buggenhout	5.3829***	210
	-----		
	Total	3.6476***	1567

The mean pH-values under forest cover vary with the location : they reach the highest level at Gontrode ( = 4.89 ) and the lowest at Buggenhout (4.44).

There is further a fairly great difference in mean pH-value for precipitation-water collected under a cover of conifers ( pH = 4.54 ) and under a cover of hardwoods ( pH = 4.84 ). As for the hardwood-canopy, important differences between species are observed ( Tab. 1 ; Tab. 4 ).

- The highest values are measured under alder and ash, not significantly different from each other or compared separately with the situation in free field.
- The values for beech, oak and scots pine are lower than those for the free field.
- The pH-values under oak are higher than those under a cover of beech or scots pine. Between the latter species no significant differences seem to exist.

Those observed gross differences are mainly confirmed for each location separately.

Gontrode : The difference ash/oak, ash/beech, alder/beech and oak/beech are confirmed. No significant differences are observed for ash/alder and alder/oak as well as between the free field and resp. ash, alder and oak. Between beech and the free field a highly significant difference exists ( Tab. 1 ; Tab. 5 ).

Tab. 4 : t-values for comparison in pairs of mean pH-values of rain-water for different kinds of hardwood forest cover ( cfr. Tab. 1 ) (df = degrees of freedom).

	Alder	Free field	Oak	Beech	Scots Pine
Ash	1.7020 df = 377	2.4294* df = 655	4.5124*** df = 493	6.3381*** df = 457	5.8401*** df = 353
	Alder	.2131 df = 646	2.7611** df = 484	4.9584*** df = 448	4.7578*** df = 344
		Free field	3.3436*** df = 761	6.2834*** df = 726	5.7457*** df = 622
			Oak	2.8438** df = 564	2.8166* df = 460
				Beech	.2904 df = 424

Tab. 5 : t-values for comparison in pairs of mean pH-values of rainwater in different situations at Gontrode ( cfr. Tab. 1 ) ( df = degree of freedom ).

	Free field	Alder	Oak	Beech
Ash	1.2029 df = 421	1.7020 df = 377	2.6973** df = 421	5.4712*** df = 385
	Free field	.6927 df = 512	1.7820 df = 456	5.1720*** df = 420
		Alder	.9876 df = 412	4.2206*** df = 378
			Oak	3.5111** df = 420

Buggenhout : The differences between oak and beech are insignificant (  $t = 1.3346$  for  $df = 142$  ), but the values for the free field are higher as for the beech canopy (  $t = 5.2829^{***}$  for  $df = 216$  ) and for the oak canopy (  $t = 6.1999^{***}$  for  $df = 144$  ).

Wachtebeke : The mean pH-values for the free field (4.89) and under a cover of scots pine ( 4.54 ) are highly and significantly different from each other (  $t = 3.7617^{***}$  ).

For each location separately the mean pH-value of rainwater is lower under a cover of oak, beech or scots pine than in the free field. The difference oak/beech, however, seems to be of local importance.

#### 1.4. Variation in time

Measurements, executed within a short time after rainfall starts ( parallel analysis ) and at 16 irregularly spaced time-points are more suitable to detect variations in time of mean pH-values as systematic measurements, executed with a regular interval of 2 weeks and at 9 time-points.

Method	Mean pH	Variance	Coeff.of variance/%
Systematic an.	4.730	0.208908	4.42
Parallel an.	4.860	0.609904	12.55

In the case of parallel analysis peak-values are also more pronounced and thus reflect variations more accurately ( Fig. 2 ).

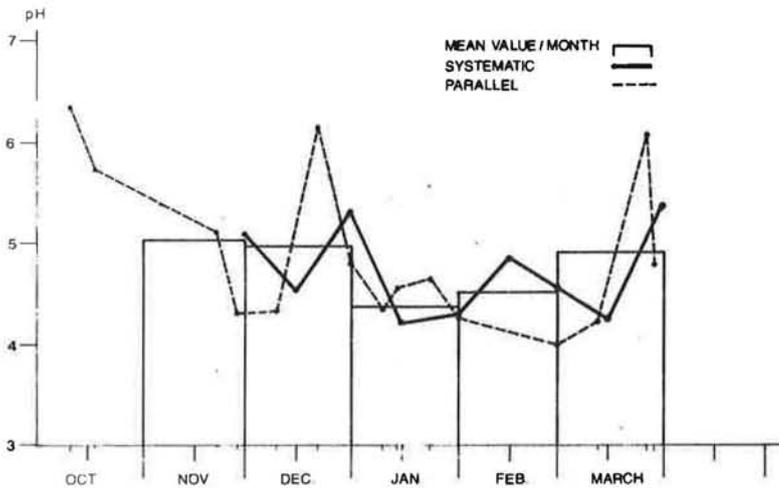
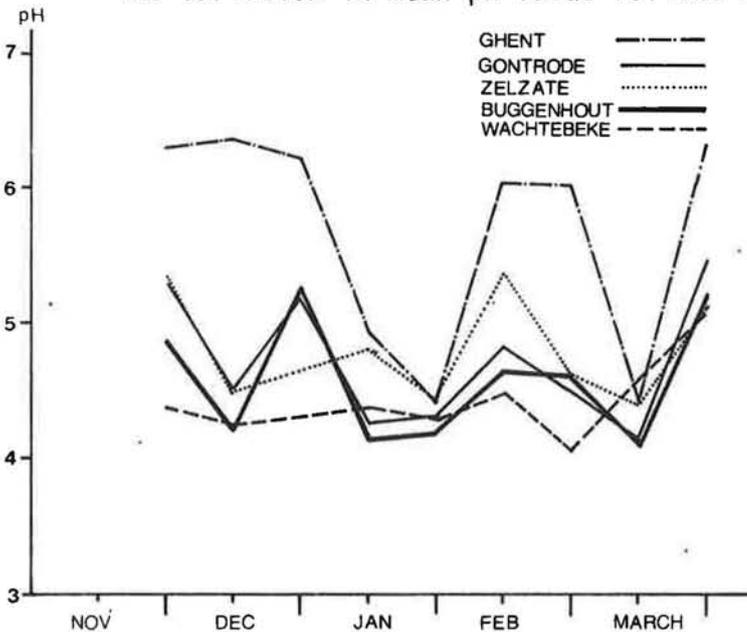


Fig. 2 : Variation in time of mean pH-values without distinction of location or particular conditions.

a. Location

The variation in mean pH-value follows the same time-pattern in each of



the 5 locations : relative maxima in the second half of december, first half of february and second half of march; relative minima during the second half of january and the first half of march ( Fig. 3 ).

Important variations in time correspond to higher mean pH-levels ( Ghent ); the least important variations in time correspond to the lowest mean pH-levels ( Buggenhout and Wachtebeke ).

Fig. 3 : Variation in time of mean pH-values at each of the 5 locations without distinction of particular conditions.

b. Forest canopy

Variation in mean pH-value follows the same pattern in the urban zones as in the free field or under forest canopy ( Fig. 4a.b.). In accordance with the already observed importance of the level of pH-value, variation in time is maximal in the urban zones and more important in the free field than under forest cover. Also in this case observed variations and peak-values are more important and thus more accurately registered by measurements, executed within a reasonable laps of time after rainfall starts.

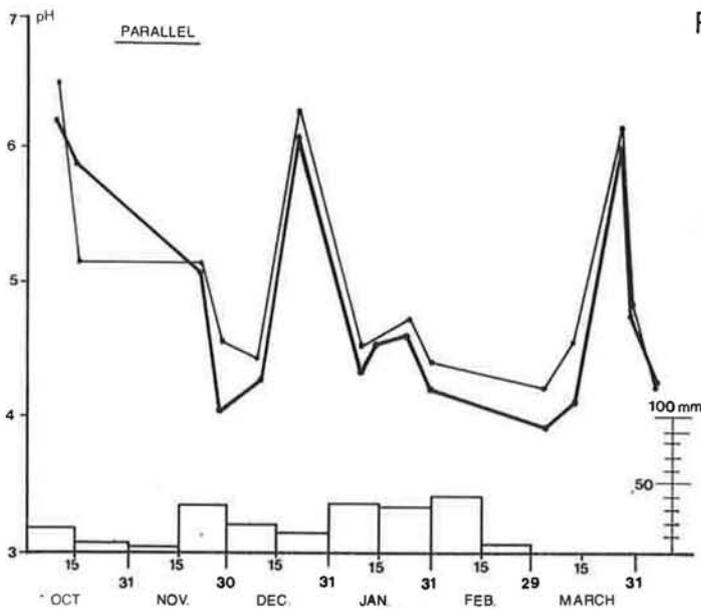
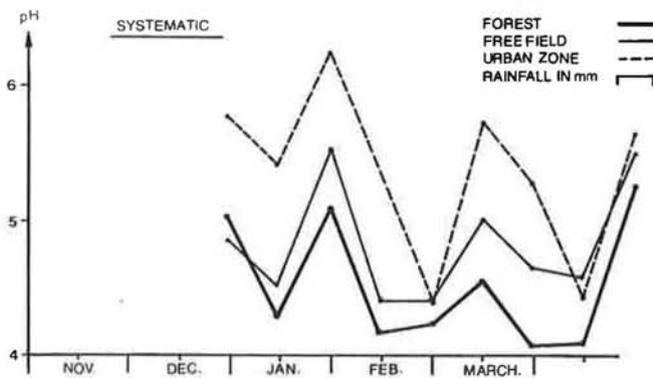
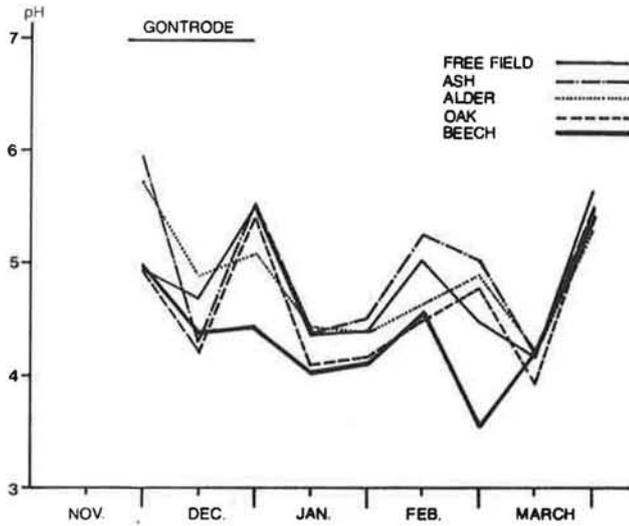


Fig. 4 : Evolution in time of mean pH-value under different general conditions but without distinction between locations. ( a.systematic measurements ) ( b. parallel measurements ).

c. Tree species



Under every type of forest cover the time-variations, already observed in a general context, are confirmed. The differences free field/forest cover and the relative differences between tree species remain, practically, unchanged in the course of time ( Fig. 5 ). The variability of mean pH as a function of time is, also under forest cover, clearly linked to the level of pH-value.

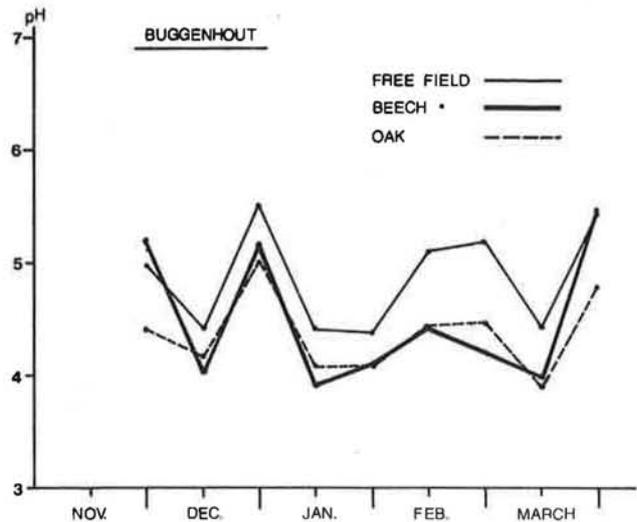
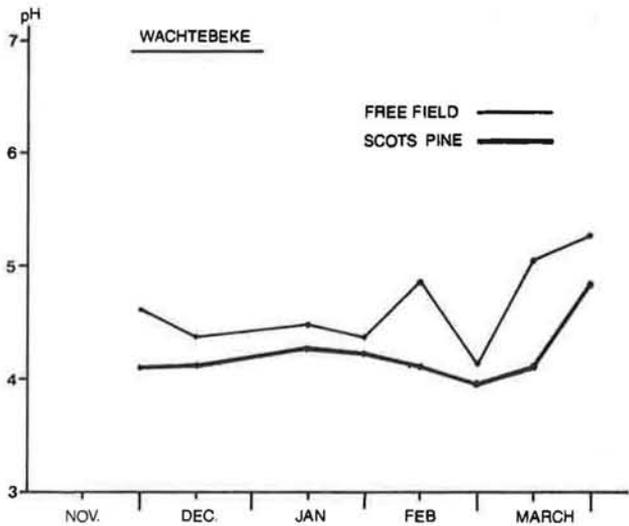


Fig. 5 : Variations in time of mean pH-value under different forest cover and in the free field at Gontrode, Wachtebeke and Buggenhout ( systematic measurement ).

2. Mineral content of rainwater

Chemical analysis of the rainwater is restricted to the quantitative determination ( mg/l ) of SO<sub>4</sub>, NO<sub>3</sub>, P, Cl, Na, K, Ca, Mg, Pb and Al of rainwater produced by direct precipitation. To this end, the contents of the 8 recipients at each observation point are mixed to make a single sample. As a consequence, the number of observations is lower as was the case for pH-measurements and this has consequences for statistical interpretation of the results ( Tab. 6 ).

Tab.6 : Average mineral content of rainwater

Minerals	mg/l	maximal peak-value	variance	var.coeff.
SO <sub>4</sub>	18.76	290.47	1207.65	1.858
NO <sub>3</sub>	3.84	19.44	28.7734	1.397
P	.136	5.51	.232472	3.545
Cl	7.70	78.15	139948	1.536
Na	2.54	81.90	63.4165	3.135
K	3.90	24.25	25.1621	1.286
Ca	.998	7.54	1.84683	1.362
Mg	17.94	111.58	524.028	1.276
Al*	.09	.93	.003218	.630
Pb	.003	.11	.000208	.481
Number of analysis : 142				

2.1. Sampling method

No significant differences in mineral content of rainwater are observed by using either the systematic or the parallel method of sampling ( K excepted ). Certain trends, however, deserve appropriate attention.

Higher concentrations of SO<sub>4</sub>, K and Ca are observed in rainwater under hardwoodcover if the systematic method of sampling is used, although really significant differences only exist for K ( t = 2.052\*; df = 79 ). Under pine-cover higher SO<sub>4</sub>-conceptions, but lower concentrations of Ca and K are found by using systematic sampling. Under free field-conditions higher values for SO<sub>4</sub>, K and Ca are measured by parallel sampling this is also the case for Na under all circumstances.

## 2.2. Spatial variation

Gross mean values for mineral content of rainwater indicate important differences between the 5 geographic locations ( without distinction of local condition or moment of sampling ), although they are statistically not really significant ( Tab. 7 ).

They allow, nevertheless, to make some provisional observations :

- The lowest values for  $SO_4$ ,  $NO_3$ , Cl, Na and K are measured in Ghent ( urban area ).
- The highest values are found in Zelzate and Wachtebeke, situated in or near an industrial area.
- The mineral content of rainwater is relatively low in the forest area of Gontrode. This is not the case for the forest area of Buggenhout, where especially high values for K and P are observed.

## 2.3. Influence of the forest canopy

### General influence

Higher concentrations of mineral elements are found in rainwater collected under a forest canopy in comparison to the values, representative for the adjacent free field ( Tab. 7 ). A considerable degree of variability is observed. The differences forest cover/free field are highly significant for Na, Ca and Mg, but especially for K and  $SO_4$  ( Fig. 6 ).

	Mineral content mg/l		t-test df = 115	Content under forest cover if " free field " = 100
	<u>Free field</u>	<u>Forest cover</u>		
$SO_4$	10.56	22.18	2.200*	210
Na	4.28	7.70	2.5942*	180
K	.667	3.53	2.5675*	528
Ca	2.50	4.09	2.1316*	164
Mg	.55	1.08	2.997**	195

Tab. 7 : Mineral content of rainwater (mg/l) at 5 locations and under specific local situations.

	GONTRODE						WACHTEBEKE		BUGGENHOUT				GHENT	ZELZATE
	F.F.	Oak	Beech	Ash	Alder	Total Forest	F.F.	Pinus	F.F.	Oak	Beech	Total Forest		
SO <sub>4</sub>	12.10	22.21	22.90	12.09	8.94	16.65	8.09	63.68	10.80	15.71	24.93	20.32	10.69	24.13
NO <sub>3</sub>	2.78	4.06	4.92	2.97	2.94	3.73	2.58	7.68	3.53	3.15	5.50	4.32	3.39	5.14
P	.064	.059	.114	.095	.085	.087	.067	.183	.094	.068	.791	.429	.085	.188
Cl	12.77	18.45	20.78	10.99	13.97	15.87	13.72	48.77	10.50	13.63	27.45	20.54	12.33	35.42
Na	4.49	8.06	8.52	3.92	5.02	6.40	5.59	27.28	3.47	5.03	11.43	8.23	5.12	19.35
K	1.05	2.66	2.72	1.63	3.57	2.63	.279	3.59	.24	1.98	12.40	7.19	.565	2.40
Ca	2.90	4.11	4.43	3.07	3.14	3.70	2.56	8.69	2.113	4.16	4.70	4.43	3.77	6.33
Mg	.608	1.16	1.20	.605	.723	.924	.646	2.75	.450	.855	1.70	1.28	.680	1.94
Al	.140	.127	.072	.026	.054	.070	.045	.363	.023	.039	.080	.059	.039	.202

There are indications that, globally, higher concentrations of  $\text{NO}_3$ , P and Cl are found under a forest canopy, but observed global differences with the free field are statistically not significant.

	Mineral content mg/l		t-test df = 115	Content under forest cover if " free field " = 100 "
	Free field	Forest cover		
$\text{NO}_3$	2.86	4.08	1.3048	143
P	.158	.738	.9353	214
Cl	12.3	18.4	1.8600	150

On the other hand, enrichment of rainfall with mineral elements is more pronounced under a pine-cover ( presence of needles ) as under a cover of hardwoods in the defoliated phenophase.

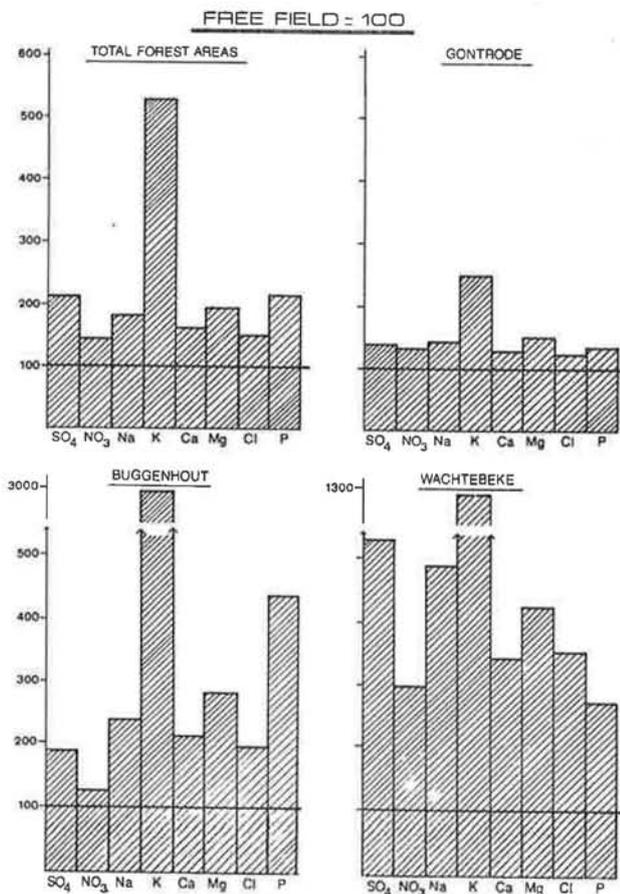


Fig.6 : Mineral content of rainwater under forest canopy for " free field " = 100.

free field. The differences are significant for P, K, Na and Mg; they are nearly significant for all other elements.

### Gontrode

The differences in mineral content of rainwater is clearly linked to the type of forest cover. The highest concentrations of  $\text{SO}_4$ ,  $\text{NO}_3$ , P, Cl, Na, Ca and Mg are reached under beech and oak. Relatively low values are measured under ash and alder : the mean concentration of  $\text{SO}_4$  (alder) or Cl and Na (ash) are below the free field-level. It is not excluded that the age of the stands has a certain importance in this respect, as well as the developmental stage, they have reached. On the other hand, only for K do statistically significant differences exist (  $t = 2.0120^*$  ;  $df = 93$  ) between the free field (1.05 mg/l) and all cover-situations together (2.63 mg/l).

### Wachtebeke

The mineral content of rainwater, collected under a pine-canopy, is higher than in rainwater, collected in the

t-values ; df = 23

SO <sub>4</sub>	NO <sub>3</sub>	P	Cl	Na	K	Ca	Mg
1.9219	1.8143	2.2760*	2.0327	2.1034*	2.6109*	1.5693	2.1352*

### Buggenhout

With the exception of P and NO<sub>3</sub> under oak-canopy, the concentrations of all other elements is higher under a forest cover as compared to the situation in the free field. Concentrations are also higher under beech than under oak.

Most remarkable are the high K-concentrations under beech and oak as well as the relatively high P-concentration under beech.

### 2.4. Variation in time

Variations in time exist, but their real importance is not yet sufficiently studied. Eventual difference and peak-values, are, also in this case, more pronounced if measurements are made within a short time after rainfall starts.

The differences forest/free field are permanent in character but the relative values, representative for each basic situation, are variable in time.

Minimal values for mineral concentrations in rainfall were found in january. A general enrichment of rainwater with mineral elements and an increase in the differences forest/free field was noticed in the first half of november and the second half of february.

Because of incomplete information on the real nature of external influences, a correct interpretation of these variations in time is not yet possible.

### 3. Conclusions

The pH of rainwater is highly variable according to geographic location, ecological situation and moment of sampling. For individual measurements it varies between 3.33 and 7.94.

In a general way the highest pH-values are found in the urban zone. pH-values are lower under oak, beech and pine as in the free field, where the situation is nearly the same as under ash and alder. The variations in pH are clearly linked to the general level of acidity :

they tend to be more important with increasing pH-value.

Concerning the mineral content of rainwater important differences between locations and ecological conditions exist. Higher concentrations of minerals are found in rainwater, collected under a forest canopy, as in the free field or in the urban zone of Ghent where the concentration of minerals reaches the lowest level. More research is needed to explain this phenomenon as well as the differences between rainwater collected under different types of forest cover ( increasing concentrations ash, alder < oak < beech < pine ).

Al-concentration is extremely low in all samples.