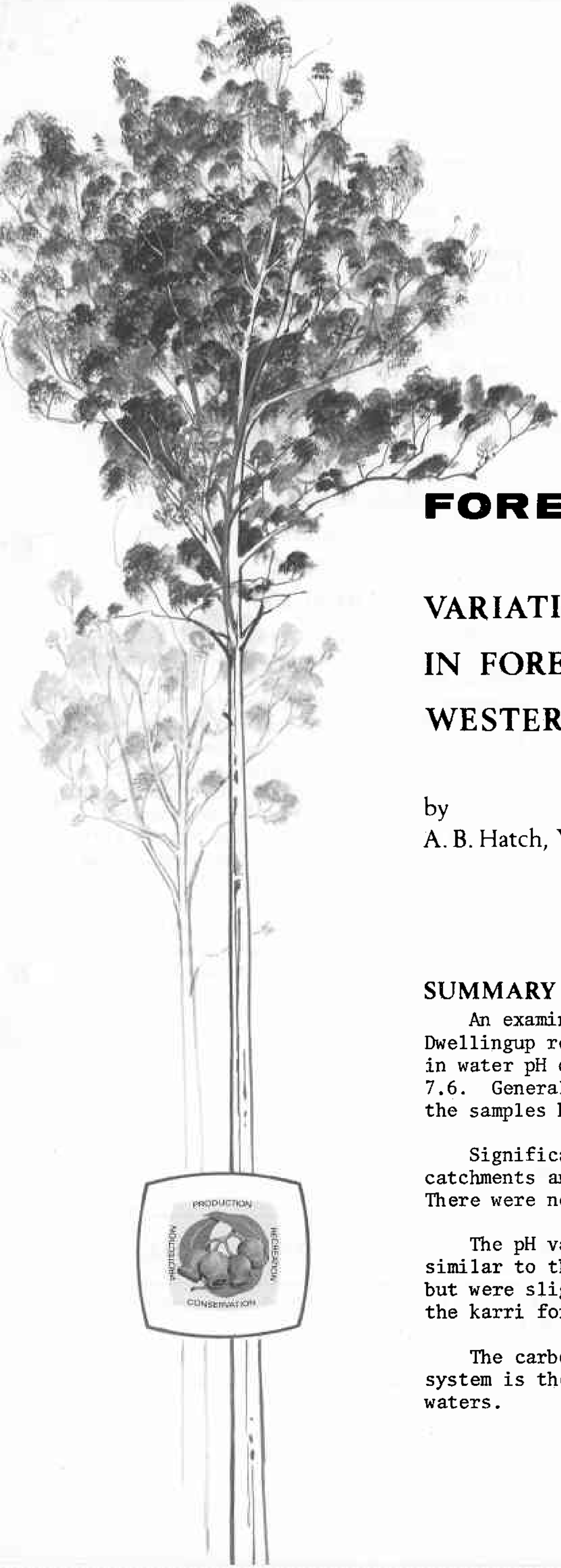

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VARIATION IN SURFACE WATER pH IN FOREST CATCHMENTS IN WESTERN AUSTRALIA

by
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SUMMARY

An examination of the forest stream waters in the Dwellingup region showed that a considerable variation in water pH occurred, with values ranging from 4.4 to 7.6. Generally the waters were slightly acid and 86% of the samples had pH values between 6.0 and 7.0.

Significant differences were observed between the catchments and also between samples from different years. There were no marked seasonal trends in pH values.

The pH values of the Dwellingup streams were similar to those observed at Mundaring and Busselton, but were slightly lower than corresponding pH values in the karri forest streams at Manjimup.

The carbon dioxide-bicarbonate-carbonate buffer system is the major factor influencing the pH of the waters.

INTRODUCTION

A detailed study of forest hydrology in Western Australia was commenced in 1973. Initially the programme was concerned with the variation in water quality in the Dwellingup forest region, 80 km south of Perth, and a large-scale sampling programme was commenced to examine some of the chemical properties of the different stream waters.

The electrical conductivity (EC) of the water was used as the main criterion for examining the different waters, but in addition detailed chemical analyses, including pH, were carried out on selected samples from the major Dwellingup catchments, viz: Davies Brook, South Dandalup River, Swamp Oak Brook and Yarragil Brook. The location of these catchments and the general features of the associated jarrah (Eucalyptus marginata Sm.) forest environment have been described by Shea et al. (1975). Some preliminary results of this work have also been described by Shea et al. (ibid.), Hatch (1976) and Shea and Hatch (1976).

The data presented in this paper show the variations in water pH observed in the Dwellingup forest catchments and a comparison of these data with those of other catchments within the forest zone. The data cover the period July 1973 to June 1976.

METHOD

Weekly stream sampling was carried out from a number of fixed points during the period of flow. The pH of the water samples was determined with either a Metrohm or Phillips pH meter using a combined glass and calomel reference electrode. Saturated potassium hydrogen tartrate (pH 3.57) and potassium dihydrogen orthophosphate-disodium hydrogen orthophosphate (pH 7.17) were used as the reference buffer solutions.

The number of samples analysed during the period were:

Davies Brook	320
South Dandalup River	528
Swamp Oak Brook	301
Yarragil Brook	439

RESULTS

The variations in water pH in the four catchments throughout the sampling period have been arranged as frequency diagrams and are tabulated in Appendixes 1 - 4. The weighted mean pH values are shown in Table 1 and from these data it is evident that considerable variation in pH occurred throughout the region with extreme values of 4.4 and 7.6 recorded. However, the majority of the waters were slightly acid and 86% of the samples had pH values between 6.0 and 7.0.

Using the mean values a simple analysis of variance showed that the pH differences between catchments were significant (Table 2).

TABLE 2

Analysis of variance
Mean pH values

Source	df	SS	MS	VR	Sig
Between catchments	3	3.5211	1.1737	11.41	***
Within "	104	10.7044	0.1029		
Total	107	14.2255			

TABLE 1

Dwellingup Catchments
Mean pH values

Year	Month	pH			
		Davies Brook	South Dandalup River	Swamp Oak Brook	Yarragil Brook
1973	July	6.60	6.39	6.50	6.67
	August	6.31	6.37	6.55	6.51
	September	6.48	6.37	6.58	6.48
	October	6.53	6.55	6.70	6.63
	November	6.83	6.68	6.87	6.82
	December	6.94	6.23	7.06	7.10
1974	January	7.04	6.57	7.05	7.40
	February	6.92	**	6.78	**
	March	6.92	**	7.11	**
	April	6.71	**	6.78	6.74
	May	6.66	**	6.68	6.74
	June	6.36	6.49	6.53	6.69
	July	6.43	6.46	6.57	6.61
	August	6.43	6.54	6.68	6.65
	September	6.72	6.62	6.89	6.91
	October	6.75	6.73	6.96	6.61
	November	6.71	6.58	6.76	6.87
	December	6.46	6.30	6.52	6.70
1975	January	6.59	6.22	6.55	**
	February	6.70	6.35	6.55	**
	March	6.49	6.18	6.40	**
	April	6.28	6.06	6.20	**
	May	6.06	5.80	6.10	**
	June	5.84	5.55	5.90	**
	July	6.40	5.89	*	6.03
	August	*	5.84		5.99
	September		5.81		5.90
	October		5.94		6.17
	November		6.08		6.22
	December		5.93		6.32
1976	January		5.72		6.08
	February		5.70		6.20
	March		**		6.20
	April		5.85		6.35
	May		6.03		6.37
	June		5.75		6.28

* Sampling completed
** Sampling points dry

TABLE 3

pH values
Between-year variation
One way classification, F values

Catchment	No. of years	df	F	
Davies Brook	3	2 + 22	4.28	*
South Dandalup River	4	3 + 27	27.92	* * *
Swamp Oak Brook	3	2 + 21	10.65	* * *
Yarragil Brook	4	3 + 24	20.68	* * *

Similarly, the pH differences for each catchment between years were significant (Table 3).

The most complete data available were for the periods July-December in 1973 and 1974. These periods cover the drying cycle for the streams: during the winter months runoff is largely due to surface flow, whereas during the drier late spring-early summer months the runoff is predominantly through subsoil seepage (base flow). Significant changes in other water properties (EC and chloride) have already been reported during these drying cycles (Hatch, <u>op. cit</u>.).

The analysis of variance for the four catchments is shown in Table 4 and these data support the general conclusion drawn from Table 2: the differences between the catchments were significant. However, over the two-year period the differences between years were not significant. The seasonal effects shown by months were also highly significant and there was a strong interaction between years and months.

The seasonal trends observed in pH values were very irregular but there was an indication that the summer pH means were slightly higher than the corresponding winter values.

As part of the forest hydrology project a drilling programme was carried out in the major catchments to examine the distribution of salt and water throughout the soil profile. This programme revealed the presence of permanent aquifers in the deeper sections

TABLE 4

Effect of time on stream pH
Analysis of variance

Source		df	SS	MS	VR	Sig
Catchments	(C)	3	0.4442	0.1481	14.66	* * *
Years	(Y)	1	0.0105	0.0105	1.04	NS
Months	(M)	5	0.3840	0.0768	7.60	* * *
C x Y		3	0.0295	0.0098	0.97	NS
C x M		15	0.3252	0.0217	2.15	NS
Y x M		5	0.5076	0.1015	10.05	* * *
C x Y x M		15	0.1513	0.0101		
Total		47	1.8523			

of the lateritic profile. The summarised pH data for the soil water from the bores are shown in Table 5 and it is evident that the subsurface waters are more acid than the stream waters. These low pH values are generally not reflected in the pH of the surface streams and it is concluded that under current forest conditions the water in the aquifers has little effect on the pH of the surface stream waters.

As pH was not previously considered to be an important water parameter in the forest streams only limited data are available from other areas. The mean monthly pH values for a number of streams from Mundaring, Busselton and Manjimup are shown in Table 6. These regions occurred over a geographic range of 280 km and included a wide range of soil and vegetation types (e.g. jarrah, karri (E. diversicolor F. Muell.) and wandoo (E. wandoo Blakely)). Generally the pH values of streams at Mundaring and Busselton were similar to those at Dwellingup, but the karri forest streams at Manjimup showed significantly higher pH levels. These higher pH levels are attributed to the leaching of the heavy karri forest litter which is higher in total bases than either of the other two species.

TABLE 5

Dwellingup bores
pH values

Year	Month	pH	
		Mean	Range
1975	July	5.65	4.9 - 6.1
	August	5.79	4.7 - 6.6
	September	5.82	4.7 - 6.8
	October	6.13	5.4 - 6.6
	November	5.92	5.4 - 6.6
	December	5.84	4.9 - 6.8
1976	January	5.62	4.8 - 6.2
	February	5.84	4.6 - 6.7
	March	5.55	4.4 - 6.4
	April	5.25	3.8 - 6.0
	May	5.35	3.6 - 7.0
	June	5.29	4.0 - 6.3
	July	5.60	4.5 - 6.2
	August	5.60	5.0 - 6.2

TABLE 6

Comparison of forest stream waters
pH values

		Dwellingup	Mundaring	Busselton	Manjimup
1973	September	6.48			6.76
	October	6.60			7.18
	November	6.80			7.33
	December	6.83			7.56
1974	July	6.52	6.68		
	August	6.58	6.80		
	September	6.78	6.94		
	October	6.76	7.12		
	November	6.73	6.92		
	December	6.50	6.64		
1975	July	6.11	6.24	5.92	
	August	5.86	6.08	6.08	
	September	5.86	6.32	5.90	
	October	6.06	6.25	6.24	
	November	6.15	6.41	6.36	
	December	6.12	6.67	6.10	

DISCUSSION

The principal factors affecting the pH of the water are: the amount and composition of the salts dissolved in the water; and the effect of the ionization of the carbonic acid formed by the solution of atmospheric carbon dioxide in the water. In natural waters which do not show marked extremes in pH the buffer system:

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{--}$$

is the chief factor regulating the pH of the water (Hart, 1974). In all waters examined the carbonate ion must be absent because free carbonate ions cannot exist in solution below pH 8.3 (Vogel, 1962).

The EC of the waters showed a wide variation with values ranging from the minimum of 10 $mS \cdot m^{-1}$ in July to a maximum of 2000 $mS \cdot m^{-1}$ in January. This parameter is closely correlated with the soluble salts present in the water; therefore, it is concluded that the soluble salt concentration does not have a significant effect on the water pH.

Detailed analyses of stream waters have shown that all the waters have a similar mean ionic composition, viz:

calcium	6%	chloride	86%
magnesium	21%	bicarbonate	9%
potassium	1%	sulphate and other anions	5%
sodium	72%		

The cationic composition was remarkably constant throughout the year over the whole range of EC values observed. The anionic composition was slightly more variable due to changes in the proportion of bicarbonate which tended to reach a maximum value during the winter months. During the sampling period water temperatures varied from 7 to 26°C and this temperature range has a large effect on the solubility of atmospheric carbon dioxide in the water.

With the observed ionic composition the principal salts present in the water are the chlorides and bicarbonates of the common alkali (Na, K) and alkaline earth (Ca, Mg) elements. Dilute solutions of the chlorides of these elements tend towards electrical neutrality and their pH is close to a value of 7. Therefore, the hydrolysis of the bicarbonate salts is the major factor controlling the pH of the water.

It was observed in laboratory tests that distilled water in equilibrium with the atmosphere had a pH of 5.4, so the presence of the other ions in the water tended to buffer the pH of the water towards neutrality.

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APPENDIX 1

Davies Brook Catchment
pH distribution

Year	Month	5.2	5.3	5.4	5.5	5.6	5.7	5.8	5.9	6.0	6.1	6.2	6.3	6.4	6.5	6.6	6.7	6.8	6.9	7.0	7.1	7.2	7.3	7.4	Sums	Means
		pH class																								
		No. of observations																								
1973	July															1									1	6.60
	August	1	1	1						1	2	5	5	4	7	5		1		1					34	6.31
	September											3	5	1		1	4	1	1						16	6.48
	October												3	2	1	4	1	2							13	6.53
	November													1	1	1	1	1	2		2		1		10	6.83
	December													1				1	1	2		1	1		7	6.94
1974	January													1					3	5	2	2	2	1	16	7.04
	February															1	1	4	3	4	1	2			16	6.92
	March															1	2	1	4	2	3	1			14	6.92
	April									1	1			2		1	2	6	3	3					19	6.71
	May												1		2	6	1	5		1					16	6.66
	June			1						1	2	1	1	1	7			1		1					16	6.36
	July											3	2	5	5	3	1								19	6.43
	August				1							2	1	2	4	4	1	1							16	6.43
	September													1		4	4	4	3						16	6.72
	October													1	1	3	4	8		2	1				20	6.75
	November												1	1	2	1	1	3	1	1		1			12	6.71
	December									1			2		1	5									9	6.46
1975	January												1		1	4	1	1							8	6.59
	February														2	1		3	1						7	6.70
	March											2			2	3	1								8	6.49
	April									1	2	2	1	2	1	1									10	6.28
	May					1		1		2	1	1		2											8	6.06
	June		1			1		2	2	1				1											8	5.84
	July													1											1	6.40
Sums		1	2	2	1	2	-	3	2	8	8	19	23	29	37	50	25	43	22	22	9	7	4	1	320	

APPENDIX 2

South Dandalup Catchment
pH distribution

Year	Month	pH class																																Sums	Means
		4.4	4.5	4.6	4.7	4.8	4.9	5.0	5.1	5.2	5.3	5.4	5.5	5.6	5.7	5.8	5.9	6.0	6.1	6.2	6.3	6.4	6.5	6.6	6.7	6.8	6.9	7.0	7.1	7.2	7.3	7.4	7.5		
		No. of observations																																	
1973	July															1	1	4		1	2	5	2	11	1									28	6.39
	August													2	1	1	6	7	4	7	7	24	20	17	10	2								108	6.37
	September															1	2		4	3		6	3		3	1	1	1						25	6.37
	October																	1		3	1	3	3	2	5	5	1							24	6.55
	November																1		1	1		1	4	1	2		1	2		1	1		1	17	6.68
	December	1			1																2				2	1	1				1			9	6.23
1974	January			1																1				1		1	1					1	1	7	6.57
																																		-	-
	May																			1	1	1	2	1		1		1						8	
	June													2				1		1	1	3	2	6	3	4		1						24	6.49
	July																	2	2		3	5	6	7	4	1								30	6.46
	August																		1	2	2	2	4	5	4	4								24	6.54
	September																			2		1	5	6	2	6	2							24	6.62
	October																			2		2	3	6	3	5	2	4		3				30	6.73
	November															1				2		3		2	1	1	4	1						15	6.58
	December																			5		3	1											9	6.30
1975	January																		1	2		1												4	6.22
	February																			1	1	1	1											4	6.35
	March																		2	1	1													4	6.18
	April																1	2		2														5	6.06
	May												1							1														2	5.80
	June											2		1		1																		4	5.55
	July					1	1							3	5	3		6	1	6	1	1	1											29	5.89
	August										1			2	4	5	4	2	1							1								20	5.84
	September												2	1	2	7	3	4																19	5.81
	October									1			1	1		4	2	8	5	1				1										24	5.94
	November													1			1	1	4	3		1												11	6.08
	December												2			1				2		1												6	5.93
1976	January													1	1	2																		4	5.72
	February														1																			1	5.70
	March																																	-	-
	April													1					1															2	5.85
	May																1	1		1														3	6.03
	June													2		1		1																4	5.75
	Sums	1	-	1	1	1	1	-	-	1	1	2	6	17	14	28	22	40	27	51	22	64	57	66	40	33	13	10	-	4	2	1	2	528	

APPENDIX 3

Swamp Oak Brook Catchment
pH distribution

Year	Month	5.7	5.8	5.9	6.0	6.1	6.2	6.3	6.4	6.5	6.6	6.7	6.8	6.9	7.0	7.1	7.2	7.3	7.4	Sums	Means
		pH class																			
		No. of observations																			
1973	July								1		1									2	6.50
	August						3	4	12	17	14	5	6	5						66	6.55
	September						2		3	5	3	1	4	2						20	6.58
	October									3	2	4	5		1					15	6.70
	November									1	1	1	2	2	1		1	1		10	6.87
	December													1	2	1		1		5	7.06
1974	January											1	2		3	3	1		2	12	7.05
	February								1			2	3		2					8	6.78
	March													1	3		3		1	8	7.11
	April								1		2	2	3	2	1	1				12	6.78
	May							1	1	2	4	1	4	1	2					16	6.68
	June					1		2	3	1	5	1	3							16	6.53
	July				1				1	4	10	2	2							20	6.57
	August										8	4	4							16	6.68
	September										1		5	4	4	1				15	6.89
	October											1	5	5	5		3	1		20	6.96
	November									2	2	1	1	1	3					10	6.76
	December								1	2	2									5	6.52
1975	January								1		3									4	6.55
	February									2	2									4	6.55
	March								4											4	6.40
	April				1		3		1											5	6.20
	May		1				3													4	6.10
	June	1	1		1	1														4	5.90
	Sums	1	2	-	3	2	11	7	30	39	60	26	49	24	27	6	8	3	3	301	

APPENDIX 4

Yarragil Brook Catchment
pH distribution

Year	Month	5.6	5.7	5.8	5.9	6.0	6.1	6.2	6.3	6.4	6.5	6.6	6.7	6.8	6.9	7.0	7.1	7.2	7.3	7.4	7.5	7.6	Sums	Means
		pH class																						
		No. of observations																						
1973	July									2	2	6	3	2								1	16	6.67
	August						1	3	5	18	21	19	9	2	1	1							80	6.51
	September						2	3		5	8	1	1	2	1	1							24	
	October							2	2		1	3	3	5	1	1							18	6.63
	November										2	2	1	1	3	1		1	1				12	6.82
	December															2		2					4	7.10
1974	January																	1		1		1	3	7.40
	February																						-	
	April											1	1	3									5	6.74
	May										1	1	1	4	1								8	6.74
	June									2	2	3	5	7			1						20	6.69
	July									2	4	11	5	3									25	6.61
	August									3	1	6	4	5	1								20	6.65
	September											1	2	3	4	7	2						19	6.91
	October										1	1	1	6	4	8		2	1				24	6.61
	November										1	1	1	2	2	2		2					11	6.87
	December												1										1	6.70
1975	July	1	2	4	3	3	3	2	4	1	1												24	6.03
	August			7	4	5		2	1						1								20	5.99
	September	1	3	3	5	4	3	1															20	5.90
	October			1	2	3	6	5	3	4	1												25	6.17
	November			1	2	4	2	4		1	2	4											20	6.22
	December							5			2	1											8	6.32
1976	January	1		1				1	3														6	6.08
	February							4															4	6.20
	March							1															1	6.20
	April								1	1													2	6.35
	May					1		1	1		3	1											7	6.37
	June					1	1	4	2	2	1	1											12	6.28
	Sums	3	5	17	16	21	18	38	22	41	54	63	38	45	19	23	3	8	2	1	-	2	439	