BULLETIN 89
1976

ISSN 0085-8129

SOME CHEMICAL PROPERTIES OF FOREST STREAM WATERS IN WESTERN AUSTRALIA

by

A. B. HATCH

FORESTS DEPARTMENT,
PERTH,
WESTERN AUSTRALIA.

SOME CHEMICAL PROPERTIES OF FOREST STREAM WATERS IN WESTERN AUSTRALIA

by

A. B. HATCH

B. J. BEGGS
Conservator of Forests

PERTH
1976

102395—(1)

TABLES

FIGURES

SUMMARY

The forest stream waters in Western Australia showed a wide variation in electrical conductivity (EC) throughout the region, with values ranging from 1×10^2 to 3×10^4 $\mu S \cdot cm^{-1}$. Within any particular stream there was also a marked seasonal variation in EC, with minimum values being recorded during the cool, wet, winter months when peak stream flow occurred. The maximum EC values were observed either immediately prior to the stream drying up or during the late summer months.

The EC of the waters was related to the total dissolved solids (TDS), the sum of the cations (Ca, Mg, K and Na) and the chloride concentration by a series of linear regression equations.

The cationic composition of all waters was very similar, and the mean ionic percentages were Ca - 6%, Mg - 21%, K - 1% and Na - 72%.

Chloride was the dominant anion present in the waters, and the mean ionic percentages were Cl - 86%, HCO_3 - 9% and SO_4 - 5%.

The forest streams, with their high proportion of sodium and chloride, were significantly different from overseas inland waters where, generally, calcium and sulphate are the dominant ions present.

SOME CHEMICAL PROPERTIES OF FOREST STREAM WATERS IN WESTERN AUSTRALIA

INTRODUCTION

The forest catchments in Western Australia are of fundamental importance to the water supply of the State, and extensive sampling of catchment streams for total dissolved solids (TDS) and sodium chloride has been carried out for many years (e.g. Public Works Department of Western Australia, 1972). This sampling has generally been confined to the principal streams of the various catchments, and the data have been used to provide stream flow records as well as salinity data. However, there appears to be a paucity of published data relating to the micro-catchments within a particular area and also to any variations between tributaries of a stream within a catchment.

In order to gain some information on these variations, a comprehensive stream sampling programme was commenced by the Forests Department during July 1973. Initially, the programme was concerned with the streams of the Dwellingup Division (80 km south of Perth), but recently it was expanded to cover streams at Mundaring (30 km north-east of Perth). Stream monitoring is also currently being carried out in the woodchip licence area at Manjimup (250 km south of Perth) and in the proposed pine plantation areas in the Busselton Division (200 km south of Perth).

The variations in water quality within the different catchments will be the subject of future reports. The aim of this paper is to examine some of the general chemical properties of the waters and determine any common features in waters from widely differing localities. An additional function of the study is to examine any seasonal variations in water quality, because under the typical mediterranean climate experienced throughout the forest region, peak stream flow generally occurred in the late winter months and tapered off or ceased during the dry summer period.

This work forms part of a large-scale interdepartmental project investigating the effect of environmental changes (e.g. jarrah dieback disease, bauxite mining and woodchip operations) on water quality and yield throughout the forest.

EXPERIMENTAL

Weekly samples were collected from selected streams at Busselton, Dwellingup, Manjimup and Mundaring in 100-500 ml plastic bottles and transported to the central laboratory for analysis. This paper reports results from July 1973 to November 1975.

The electrical conductivity (EC) (an excellent measure of TDS) of all samples was measured using a Phillips Measuring Bridge and a flow-through conductivity cell. Standard potassium chloride (0.01N) was used as the reference solution at a standard temperature of 25°C.

To quantify the relationship between EC and TDS a number of samples covering the range of conductivities were selected for the gravimetric determination of TDS. For this work the sample areas were divided into 2 regions: a northern (Dwellingup and Mundaring) and a southern region

(Busselton and Manjimup). The EC values for each region were stratified into 17 groups, and subsampling from each stratum for gravimetric analysis was by proportional allocation of the numbers to the different strata (Cochran, 1972). For the gravimetric analysis of TDS, suitable aliquots (25-100 ml) of these subsamples were evaporated to dryness on a water bath and dried in an oven for four hours at 105°C.

In addition to the EC measurement, key samples from each area were examined in greater detail, and for these samples the following analyses were carried out.

The pH was determined with a pH meter using a combined glass and calomel reference electrode. Saturated potassium hydrogen tartarate (pH 3.57) and sodium borate-potassium chloride (pH 9.16) were used as the reference buffer solutions.

Calcium and magnesium were determined by atomic absorption spectroscopy using strontium chloride (1 500 $mg \cdot l^{-1}Sr$) as a suppressant. The dilutions used were Ca 1 : 5 and Mg 1 : 5 or 1 : 25. The standards for both elements covered the range 0-10 $mg \cdot l^{-1}$. A check on these analyses was carried out on a range of samples by means of EDTA (ethylenediaminetetraacetic acid) titrations using the appropriate indicators (APHA, 1969; Welcher, 1958).

Potassium and sodium were estimated with an Eel Flame Photometer, using appropriate standards. For potassium, the analyses were carried out on undiluted water samples using a range of 0-8 $mg \cdot l^{-1}K$ for the standard solutions: for the sodium analyses the water samples were diluted either 1 : 20 or 1 : 400 with water prior to flaming. The sodium standards covered the range 0-10 $mg \cdot l^{-1}$ Na.

The major anion determined was chloride, and during the sampling period this was analysed by several methods:

(a) the Mohr titration (APHA, 1969; Vogel, 1968);
(b) an electrometric titration (Piper, 1947);
(c) coulometrically, with an Eel Chloride Meter;
(d) the use of a Specific Ion Electrode (Cl).

For method (d) a suitable aliquot (0.5-5 ml) of the water sample was diluted to 10 ml with water, 5 ml of molar potassium nitrate were added, and the potential developed between the chloride electrode and a calomel reference electrode read off a sensitive pH meter. The standard chloride solutions covered the range 50-500 $mg \cdot l^{-1}$ chloride.

Quantitative tests of the four methods were carried out on 13 water samples covering the range 1.2 to 67.2 $me \cdot l^{-1}$ of chloride.

Other anions determined were bicarbonate and sulphate, the former being analysed by titration of an aliquot of the sample to pH 4.4 with 0.01 N potassium biiodate, and the latter was estimated by EDTA titration (Bond, 1955; Welcher, 1958). The volumetric estimation of sulphates initially proved rather difficult due to the low concentration of the ion present in the waters; this was overcome by spiking the samples with a known amount of standard potassium sulphate solution prior to the analysis. This procedure markedly improved the accuracy of the technique and values thus obtained were in close agreement with those determined by the classical gravimetric precipitation of barium sulphate (APHA, 1969).

Ammonium, nitrate and phosphate, which are generally regarded as indicators of polluted water, were checked for in several areas throughout the sampling period. For these ions the following colorimetric techniques were used:

(a) ammonium was determined by distillation of an aliquot of the sample with either magnesium oxide or 1.0 m sodium hydroxide (1 ml), and the distilled ammonia estimated by nesslerization (APHA, 1969; Piper of CSIRO Division of Soils, unpublished data);

(b) nitrate was analysed either by the 3 : 4 xylene-1-ol technique (Piper and Lewis, 1951) or a modified manual ultraviolet spectrophotometric method (Ramirez-Munoz, 1974);

(c) phosphate was estimated by a molybdenum blue method in which ascorbic acid was used as the reducing agent (Murphy and Riley, 1962).

RESULTS

(1) Chemical techniques

(a) Calcium and magnesium

The comparison of the EDTA and atomic absorption techniques for the estimation of calcium and magnesium is shown in Table 1. Statistical analysis of the data showed that there was no significant difference between the two methods for the estimation of these two elements (Table 2). For the analysis of calcium 5 000 $\text{mg}\cdot\text{l}^{-1}$ strontium is usually recommended as a suppressant

TABLE 1

CALCIUM AND MAGNESIUM ANALYSES

Comparison of different analytical techniques

Sample No.	EC $\mu\text{S}\cdot\text{cm}^{-1}$	Ca $\text{me}\cdot\text{l}^{-1}$		Mg $\text{me}\cdot\text{l}^{-1}$	
		EDTA (a)	AA (b)	EDTA (a)	AA (b)
136	146	0·15	0·09	0·24	0·23
223	271	0·14	0·08	0·34	0·42
219	351	0·24	0·17	0·56	0·57
88AB	546	0·29	0·25	1·00	1·02
109	838	0·39	0·37	1·41	1·38
A400	1 028	0·39	0·34	1·75	1·74
95AB	1 128	0·39	0·45	1·89	1·82
137AB	1 291	0·53	0·49	2·09	2·05
1A	1 826	0·79	0·84	3·06	3·04
B492	2 600	1·34	1·38	4·58	4·48
B150	3 162	1·70	1·80	5·98	5·88

(a) Estimated by titration with EDTA
(b) Estimated by atomic absorption spectroscopy

(Varian Techtron, 1972), but the data from Tables 1 and 2 clearly indicate that for the waters sampled 1 500 $mg \cdot l^{-1}$ strontium is adequate to eliminate any interference effects.

TABLE 2

CALCIUM AND MAGNESIUM ANALYSES

Analyses of variance

Calcium

Source	df	SS	MS	VR	
Between techniques	1	0·0004	0·0004	0·001	NS
Within techniques	20	5·6535	0·2827	....	....
Total	21	5·6539	....	....	....

Magnesium

Source	df	SS	MS	VR	
Between techniques	1	0·0033	0·0033	0·001	NS
Within techniques	20	64·2762	3·2138	....	....
Total	21	64·2795	....	....	....

(b) Chloride

The data for the four analytical methods are shown in Table 3, and again statistical tests showed no significant differences between the various methods (Table 4).

TABLE 3

CHLORIDE ANALYSIS

Comparison of different analytical techniques

Sample No.	EC $\mu S \cdot cm^{-1}$	Chloride ($me \cdot l^{-1}$)			
		A	B	C	D
133A	307	1·55	1·55	1·50	1·41
A119	285	1·34	1·35	1·26	1·19
A114	348	1·94	1·93	1·88	1·74
508	415	2·58	2·59	2·53	2·45
7A	619	4·53	4·52	4·50	4·46
A101	778	6·03	6·07	6·05	6·01
95BC	768	6·07	5·93	5·99	6·28
A33	533	3·70	3·70	3·70	3·68
A109	1 496	12·73	12·85	12·49	12·01
40BC	1 750	15·25	15·26	15·13	15·18
13AB	2 241	19·86	19·93	19·98	19·62
502	2 061	18·01	18·22	18·07	17·63
A60	7 197	67·14	67·01	66·99	66·17

A Mohr titration
B Electrometric titration
C Coulometrically (Eel Chloride Meter)
D Specific Ion Electrode (Cl)

TABLE 4
CHLORIDE ANALYSIS
Analysis of variance

Source	df	SS	MS	VR	
Between techniques	3	0·463 2	0·154 4	0·000	NS
Within techniques	48	14 904·261 3	310·505 4	....	....
Total	51	14 904·724 5	....	....	....

(c) Sulphate

The check analyses for sulphate are shown in Table 5, and the statistical analysis of the data showed no significant difference between the three methods (Table 6). However, the addition of the standard potassium sulphate solution markedly improved the detection of the end point of the titration with the low sulphate samples.

TABLE 5
SULPHATE ANALYSIS
Comparison of different analytical techniques

Sample No.	EC $\mu S \cdot cm^{-1}$	Sulphate $me \cdot l^{-1}$		
		A	B	C
W2	282	0·16	0·35	0·18
W4	221	0·20	0·50	0·25
A376	523	0·21	0·25	0·25
61	776	0·22	0·40	0·25
A130	1 558	0·50	0·52	0·51
B51	1 026	0·22	0·26	0·26
C1	3 095	0·81	0·92	0·83

A gravimetric estimation
B EDTA titration
C EDTA titration after sample spiked with 5 ml of 0·003 119 M K_2SO_4

TABLE 6
SULPHATE ANALYSIS
Analysis of variance

Source	df	SS	MS	VR	
Between techniques	2	0·060 4	0·030 2	0·55	NS
Within techniques	18	0·982 3	0·054 6	....	....
Total	20	1·042 7	....	....	....

(d) Other ions

The tests for ammonium nitrogen indicated that only trace amounts of this form of nitrogen occurred in the waters examined, with the majority of samples containing less than 0.1 $mg \cdot l^{-1}$. Nitrate values were also low, generally being less than 0.05 $mg \cdot l^{-1}$. The highest value recorded was 0.98 $mg \cdot l^{-1}$ of nitrate, and this occurred in a sample with an EC value of 3 180 $\mu S \cdot cm^{-1}$ (TDS, 2 200 $mg \cdot l^{-1}$).

Phosphorus values were extremely low, being less than 0.005 $mg \cdot l^{-1}$ in all samples analysed.

As a result of these findings the concentrations of ammonium, nitrate and phosphate were not included when balancing the cations and anions present in the water.

(2) Electrical conductivity relationships

An important criterion for water quality is the concentration of soluble salts present in the water, and it is generally agreed that the EC of the water is a good measure of the TDS present (Hart, 1974; Richards, 1969).

As a preliminary step 80 samples were selected from the different conductivity strata of the Dwellingup and Mundaring samples, and analysed for TDS. The distribution of the data is plotted in Figure 1. A linear regression was fitted to these data:

$$Y = -44.743 + 0.709 X \qquad (1)$$

where Y = TDS ($mg \cdot l^{-1}$)

and X = EC ($\mu S \cdot cm^{-1}$)

Using SI values this equation becomes:

$$\text{TDS} (mg \cdot l^{-1}) = -44.74 + 7.09 \text{ EC } (mS \cdot m^{-1}). \qquad (2)$$

The analysis of variance for regression (1) is shown in Table 7.

TABLE 7

TOTAL DISSOLVED SOLIDS AND ELECTRICAL CONDUCTIVITY

Dwellingup and Mundaring samples

Analysis of variance

Source	df	SS	MS	VR	
Regression (1)	1	42 109 511·63	42 109 511·63	39 958·54	***
Deviations	78	82 198·56	1 053·83	....	....
Total	79	42 191 710·19	....	....	....

$R^2 = 0{\cdot}998$
SD = 32·463
r = 0·999 ***

Equation 1 was used for all the preliminary calculations of TDS present in the waters. However, for the later sampling from the southern region (Busselton and Manjimup) a second regression was calculated using 63

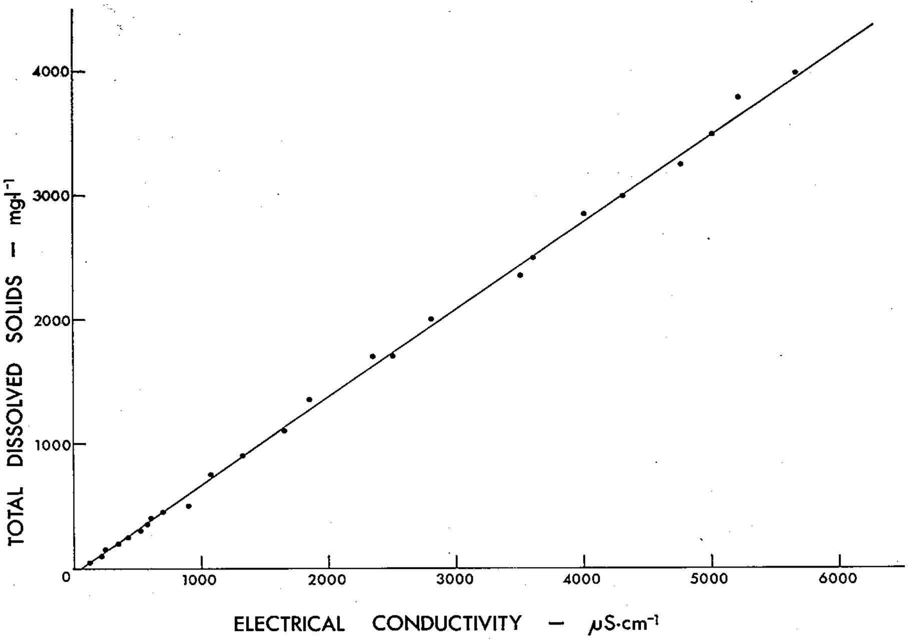

Figure 1
Relationship between total dissolved solids and electrical conductivity for Dwellingup and Mundaring streams

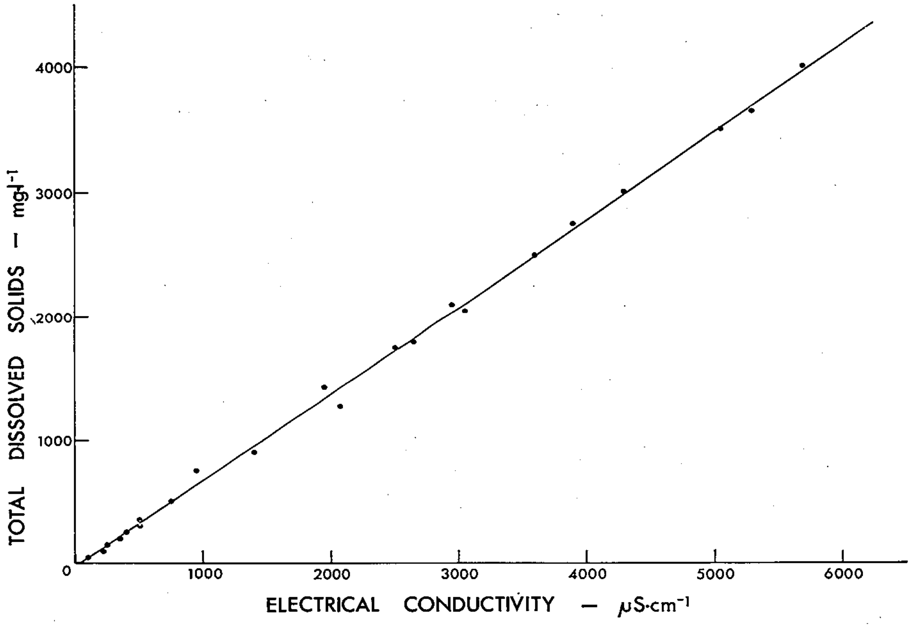

Figure 2
Relationship between total dissolved solids and electrical conductivity for Busselton and Manjimup streams

subsamples from the stratified data. These results have been plotted in Figure 2 and the equation is:

$$Y = -26.248 + 0.701\ X \qquad (3)$$

and the SI equivalent is:

$$\text{TDS}\ (\text{mg}\cdot\text{l}^{-1}) = -26.26 + 7.01\ \text{EC}\ (\text{mS}\cdot\text{m}^{-1}). \qquad (4)$$

The analysis of variance for Equation (3) is set out in Table 8.

TABLE 8

TOTAL DISSOLVED SOLIDS AND ELECTRICAL CONDUCTIVITY

Busselton and Manjimup samples

Analysis of variance

Source	df	SS	MS	VR	
Regression (3)	1	40 068 417·69	40 068 417·69	44 441·46	***
Deviations	61	54 997·87	901·60	....	....
Total	62	40 123 415·56	....	....	....

$R^2 = 0{\cdot}999$
SD = 30·027
$r = 0{\cdot}999$ ***

A comparison of the two regressions was carried out using the techniques described by Snedecor and Cochran (1973) and Williams (1959), and the results are shown in Table 9.

TABLE 9

TOTAL DISSOLVED SOLIDS AND ELECTRICAL CONDUCTIVITY

Test of homogeneity of positions and regressions

Source	df	SS	MS	VR	
Combined regression	1	82 168 537·82	82 168 537·82	....	....
Difference of regressions	1	9 391·50	9 391·50	9·52	**
Combined residual	139	137 196·43	987·02	....	....
Total within groups	141	82 315 125·75	....	....	....

Source	df	SS	MS	VR	
Overall regression	1	82 264 819·03	82 264 819·03	83 346·66	***
Difference of positions	1	374·47	374·47	0·38	NS
Difference of regressions	1	9 391·50	9 391·50	9·52	**
Combined residual	139	137 196·43	987·02	....	....
Total	142	82 411 781·43	....	....	....

This table clearly indicates there is a significant difference between the two regression slopes ($b1 = 0.709$ and $b2 = 0.701$) but the difference between the constants (a1 = -44.743 and a2 = -26.248) is not significant. However, these differences have no practical significance in the testing of water quality, so the complete data were pooled to give an overall regression which could be used to estimate TDS:

$$Y = -36.515 + 0.705 X \tag{5}$$

and the analysis of variance is shown in Table 10. The SI equivalent of Equation (5) is:

$$\mathrm{TDS}\ (\mathrm{mg \cdot l^{-1}}) = -36.52 + 7.05\ \mathrm{EC}\ (\mathrm{mS \cdot m^{-1}}). \tag{6}$$

TABLE 10

TOTAL DISSOLVED SOLIDS AND ELECTRICAL CONDUCTIVITY

Pooled data, all localities

Analysis of variance

Source	df	SS	MS	VR	
Regression (5)	1	82 264 819·03	82 264 819·03	78 927·00	***
Deviations	141	146 962·40	1 042·29	....	....
Total	142	82 411 781·43	....	....	....

$R^2 = 0 \cdot 998$

SD = 32·285

r = 0·999 ***

TABLE 11

TOTAL DISSOLVED SOLIDS AND ELECTRICAL CONDUCTIVITY

Comparison of results obtained from different equations

EC $\mu S \cdot cm^{-1}$	TDS—mg·l⁻¹					
	Dwp-Mdg (1)*	Bsn-Mjp (3)*	Pooled (5)*	G.C.L. (a)	U.S.D.A. (b)	Vic. (7)*
200	97	117	105	140	128	143
400	239	257	246	280	256	252
600	381	397	387	420	384	356
800	522	537	528	560	512	458
1 200	806	815	809	840	768	658
1 600	1 090	1 095	1 091	1 120	1 024	855
2 000	1 373	1 376	1 373	1 400	1 280	1 050

* No. refers to equations quoted in the text

(a) Using the factor 0·70

(b) Using the factor 0·64

The regression coefficients calculated in this work (0.709 and 0.701) were very similar to the value of 0.7 used by the Government Chemical Laboratories (G.C.L.) in Western Australia (Hughes of G.C.L., pers. comm.) and were slightly higher than the value of 0.64 used by the United States Department of Agriculture (U.S.D.A.) for irrigation water samples (Richards, 1969). A different relationship has been used in the analysis of Victorian waters (Australian Water Resources Council, 1969; Hart, 1974) and this equation is:

$$Y^{0.5} = 2.508 + 0.668\, X^{0.5} + 0.148 \times 10^{-4} X. \qquad (7)$$

A comparison of the relationships between TDS and EC for these different equations is shown in Table 11. It is evident from these data that the four Western Australian equations gave reasonably good agreement over the range 2 x 10^2 to 2 x 10^3 $\mu S \cdot cm^{-1}$, and the values obtained were generally higher than those obtained by the U.S.D.A. and the Victorian equations. In view of the variation obtained by the different methods it was decided to use EC values directly as a basis for classifying waters. This is in line with U.S.D.A. practice (Richards, 1969) and has the advantage that it enables a direct comparison of different water samples.

There are two other EC relationships which are useful in water studies:

(a) the relationship between the sum of the major cations (Ca, Mg, K and Na) and the EC of the water;

(b) the relationship between the chloride content and the EC of the water.

To examine these correlations 75 samples were selected from the total stratified data and linear regressions calculated. The cation–EC relationship was:

$$Y = -0.989 + 0.0105\ X \qquad (8)$$

where Y = sum of the cations, Ca, Mg, K and Na ($me \cdot l^{-1}$)

and X = EC ($\mu S \cdot cm^{-1}$).

The SI equivalent is:

$$\Sigma \text{ cations } (me \cdot l^{-1}) = 0.99 + 0.105 \text{ EC } (mS \cdot m^{-1}) \qquad (9)$$

The analysis of variance of equation (8) is shown in Table 12 and clearly indicates that the equation is an extremely good fit of the data.

TABLE 12

CATION CONCENTRATION AND ELECTRICAL CONDUCTIVITY

Analysis of variance

Source	df	SS	MS	VR	
Regression (8)	1	33 926·276 7	33 926·276 7	39 045·09	***
Deviations	73	63·431 9	0·868 9	....	....
Total	74	33 989·708 6	....	....	....

$R^2 = 0{\cdot}998$

SD = 0·932

r = 0·999 ***

The chloride–EC equation was:

$$Y = 1.364 + 0.00950\ X \qquad (10)$$

where Y = chloride concentration ($me \cdot l^{-1}$)

and X = EC ($\mu S \cdot cm^{-1}$)

and in SI units:

$$Cl\ (me\cdot l^{-1}) = -1.36 \times 0.095\ EC\ (mS\cdot m^{-1}) \qquad (11)$$

and again, this linear regression gave a good fit of the data (Table 13).

TABLE 13

CHLORIDE CONCENTRATION AND ELECTRICAL CONDUCTIVITY

Analysis of variance

Source	df	SS	MS	VR	
Regression (10)	1	30 280·211 2	30 280·211 2	25 858·42	***
Deviations	73	85·485 4	1·171 0	....	....
Total	74	30 365·696 6	....	....	....

$R^2 = 0\cdot997$
SD = 1·082
$r = 0\cdot999$ ***

The data used for the calculation of Equations (8) and (10) were analysed to calculate an additional regression line; this was the relationship between the sum of the cations and the chloride content of the water, and again, this was a linear regression:

$$Y = 0.460 + 1.058\ X \qquad (12)$$

where Y = sum of cations $(me\cdot l^{-1})$

and X = chloride concentration $(me\cdot l^{-1})$.

The analysis of variance of this equation is shown in Table 14 and this shows the close relationship between the two parameters. In addition, the equation indicates that chloride is the dominant anion present in the samples analysed.

TABLE 14

CATIONIC AND CHLORIDE CONCENTRATIONS

Analysis of variance

Source	df	SS	MS	VR	
Regression (6)	1	33 956·887 6	33 956·887 6	75 526·89	***
Deviations	73	32·821 0	0·449 6	....	....
Total	74	33 989·708 6	....	....	....

$R^2 = 0\cdot999$
SD = 0·671
$r = 0\cdot999$ ***

(3) Variations in electrical conductivity

There was a considerable variation in EC values between the different catchments and also between streams within a particular catchment. The differences within a catchment were less evident during the winter months when the maximum runoff occurred, but tended to increase as the rainfall intensity tapered off during spring and early summer. The maximum differences were generally observed immediately prior to the cessation of stream flow in ephemeral streams or during the late summer months in the permanent streams. An example of this type of variation is shown in Table 15 using data from the South Dandalup Catchment; some maximum and minimum values recorded for a wide range of sites are shown in Table 16.

TABLE 15

SOUTH DANDALUP CATCHMENT

Seasonal variation in EC between streams

Month	EC—μS·cm^{-1}						
	Sample No.						
	1	3a	7	13	16a	19a	25a
July 1973	117	209	156	254	275	179	182
October 1973	168	215	189	579	379	478	587
January 1974	207	275	297	1 119*	1 080	14 638	7 311*
April 1974	227	328	276	Dry	1 450	Dry	Dry
July 1974	149	195	138	224	254	215	293

* EC value immediately prior to the stream drying up

TABLE 16

MAXIMUM AND MINIMUM ELECTRICAL CONDUCTIVITY VALUES OF SELECTED STREAMS

Locality	Sample No.	μS·cm^{-1}			
		Minimum	Date	Maximum	Date
Busselton	1	178	23/8/74	502	17/5/74
	6	173	23/8/74	363	17/5/74
	16	153	9/8/74	512	24/1/74
	22	105	2/8/74	2 733	24/5/74
Dwellingup	AR 1	238	12/9/73	627	20/3/74
	AR 3	266	12/9/73	492	14/11/74
	DB 4	180	24/7/74	777	30/1/74
	DB 14	179	14/8/74	596	20/3/74
	MB 2	86	24/7/74	345	28/5/75
	SD 4N	130	7/8/74	467	26/2/75
	SD 10S	153	7/8/74	534	11/12/74
	SD 19 aS	134	29/5/74	30 254	5/2/75
	SO 1	249	19/9/73	749	28/5/75
	SO 10	252	17/7/74	2 678	28/3/74
	Y 4a	131	24/7/74	933	29/1/75
	Y 14	210	24/7/74	1 965	26/2/75
Manjimup	D 2	103	3/10/73	787	3/12/74
	D 5	148	26/9/73	1 865	4/2/75
	P 4	248	21/9/73	11 761	3/12/74
	P 26	1 513	27/9/73	15 116	23/4/74
	S 3	262	1/11/73	707	11/12/74
	S 22	243	3/10/73	5 153	19/2/75
Mundaring	57	269	31/7/74	1 065	23/12/74
	61	309	14/8/74	3 962	30/5/75
	120	294	8/8/74	3 010	19/6/75
	127	264	8/8/74	1 905	23/12/74

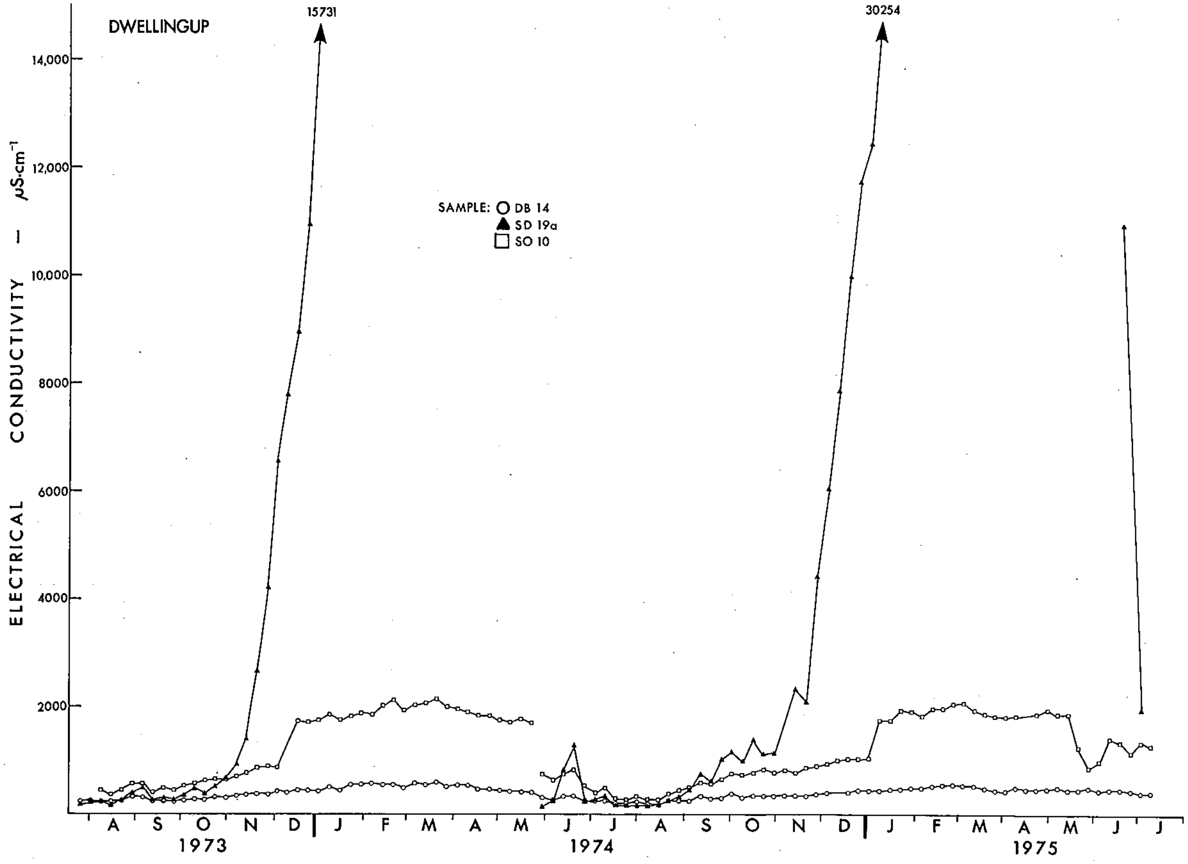

Figure 3
Seasonal variation in electrical conductivity: Dwellingup

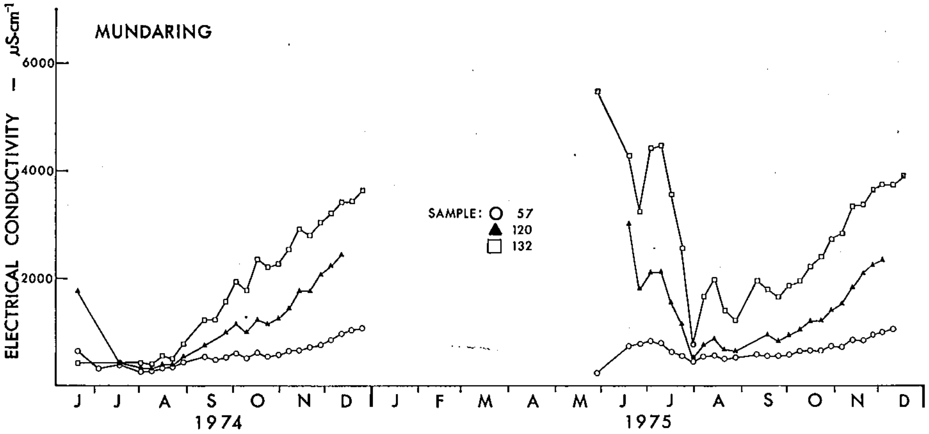

Figure 4
Seasonal variation in electrical conductivity: Mundaring

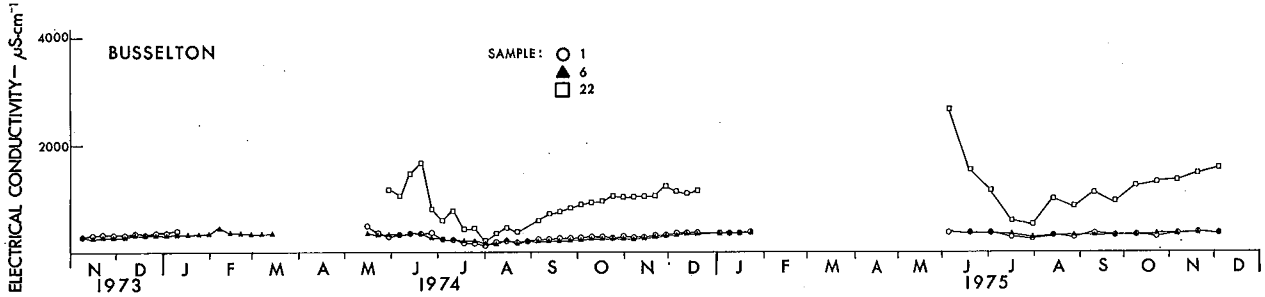

Figure 5
Seasonal variation in electrical conductivity: Busselton

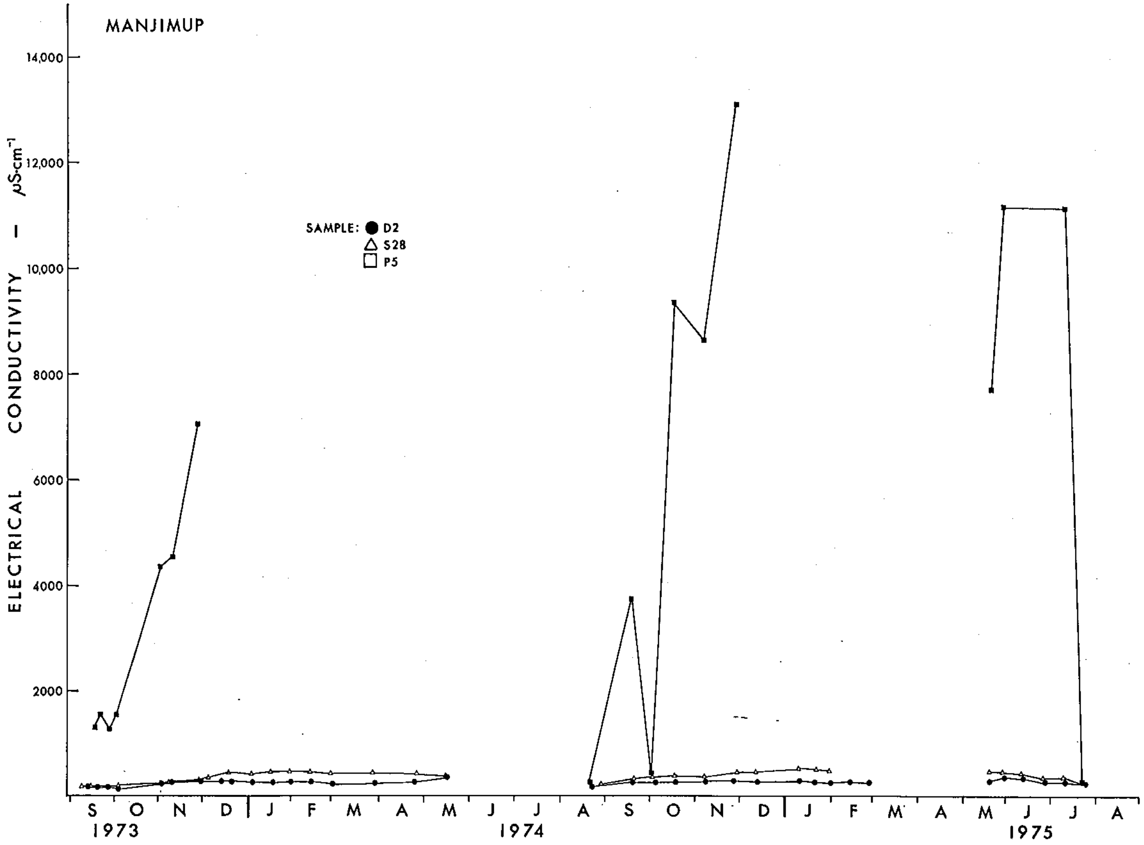

Figure 6

Seasonal variation in electrical conductivity: Manjimup

The detailed seasonal trends in EC for twelve streams are shown in Figures 3-6, and all show a similar pattern of variation throughout the year, with the minimum values being recorded during the winter months and the maximum occurring either immediately prior to the stream drying up or during the late summer months. This pattern of EC variations occurs because during the winter months the runoff is largely surface runoff, and any saline subsoil ground water is diluted by the huge excess of precipitation over transpiration and evaporation. However, during the drier spring and summer months any runoff into the streams is predominantly through subsoil seepage (base flow), and the effect of subsoil salinity becomes more pronounced.

The EC values recorded from a stream during the period of base flow are valuable indicators of the ground water salinity present in the catchment (La Sala, 1967; Pinder and Jones, 1969), but it has been suggested that these values may underestimate the amount of salts held in the subsoil profile (Shea of the Forests Department of Western Australia, pers. comm.).

The Murray River at Dwellingup is an interesting exception to the trend observed in the streams that occur within the forest zone. This river has its headwaters in agricultural country to the east of the forest zone, and in this region surface salt accumulation is quite frequent. Consequently, maximum EC values were recorded during periods of peak flow when water from the eastern agricultural zone was flowing down the River, e.g.

an EC of 7875 $\mu S \cdot cm^{-1}$ on 18.6.1975.

The minimum values were recorded in late autumn, when the River water is predominantly base flow water from the forest region, e.g.

an EC of 958 $\mu S \cdot cm^{-1}$ on 9.4.1974.

(4) Hydrogen ion concentration

The pH values recorded were independent of locality and seasonal effects, and over a wide range of samples varied between 6.1 and 7.0.

(5) Cationic composition of waters

The cationic composition of the waters was very similar throughout the forest region, and this similarity was independent of the season and the subsequent variation in stream flow. Over a wide range of samples from all localities sodium was the dominant cation, averaging 72% of the total cations (Ca, Mg, K and Na). Magnesium was next in importance, comprising 21%, and calcium and potassium were of minor importance, being 6% and 1% respectively of the total.

In association with the seasonal fluctuations in EC there was a considerable variation in the concentration of cations present in the different waters, and values ranging from 2 to 130 $me \cdot l^{-1}$ of Ca, Mg, K and Na were recorded throughout the forest. However, despite these variations in cationic concentration, the percentage composition of the cations was virtually constant throughout the year. Some examples of the variations in cationic composition are shown in Table 17, and these percentage values cover the EC range of 140 to 5 500 $\mu S \cdot cm^{-1}$.

TABLE 17

SEASONAL VARIATIONS IN CATIONIC COMPOSITION

Busselton

Sample No.	Month	EC $\mu\text{S}\cdot\text{cm}^{-1}$	%			
			Ca	Mg	K	Na
1	Jan.	387	4	22	2	72
	Feb.					
	Mar.					
	Apr.					
	May	390				
	June	277	4	20	2	74
	July	292	4	21	2	73
	Aug.	291	3	20	2	75
	Sept.	301	3	19	2	76
	Oct.	294	3	19	2	76
	Nov.	330	3	22	2	73
	Dec.	357	4	23	2	71
Mean			3·5	20·8	2·0	73·7
6	Jan.	387	3	19	2	76
	Feb.	394	4	31	2	63
	Mar.					
	Apr.	379	4	22	2	72
	May	338				
	June	349	4	22	2	72
	July	317	4	22	2	72
	Aug.	208	5	20	2	73
	Sept.	214	3	19	3	75
	Oct.	266	3	20	2	75
	Nov.	284	4	21	2	73
	Dec.	317	3	19	2	76
Mean			3·7	21·5	2·1	72·7
16	Jan.	455	3	24	2	71
	Feb.	507				
	Mar.					
	Apr.					
	May	469				
	June	329				
	July	215	8	21	2	69
	Aug.	164	7	21	2	70
	Sept.	205	4	20	2	74
	Oct.	274	4	18	2	76
	Nov.	324	4	19	2	75
	Dec.	400	3	19	2	76
Mean			4·7	20·3	2·0	73·0

Dwellingup

Sample No.	Month	EC $\mu\text{S}\cdot\text{cm}^{-1}$	%			
			Ca	Mg	K	Na
DB 14	Jan.	497	7	20	1	72
	Feb.	542	8	21	1	70
	Mar.	567	7	24	1	68
	Apr.	492	8	19	1	72
	May	391	6	18	1	75
	June	295	6	17	1	76
	July	223	5	17	2	76
	Aug.	220	6	18	2	74
	Sept.	296	7	19	1	73
	Oct.	332	6	19	1	74
	Nov.	364	7	20	1	72
	Dec.	426	7	19	1	73
Mean			6·7	19·2	1·2	72·9
SD 7	Jan.	292	9	22	2	67
	Feb.	310	4	18	2	76
	Mar.	304	5	18	2	75
	Apr.	307	6	17	1	76
	May	239	5	21	2	72
	June	297	5	19	1	75
	July	141	2	18	2	78
	Aug.	151	6	19	2	73
	Sept.	196	5	19	2	74
	Oct.	208	4	19	2	75
	Nov.	237	3	18	1	78
	Dec.	289	5	18	2	75
Mean			4·9	18·8	1·8	74·5
SO 10	Jan.	1 508	5	17	1	77
	Feb.	1 954	4	19	1	76
	Mar.	2 381	4	21	1	74
	Apr.	1 753	5	21	1	73
	May	1 510	5	20	1	74
	June	604	4	16	1	79
	July	318	3	15	1	81
	Aug.	346	5	18	1	76
	Sept.	618	5	20	1	74
	Oct.	783	5	19	1	75
	Nov.	958	5	15	1	79
	Dec.	1 306	5	22	1	72
Mean			4·6	18·6	1·0	75·8

Manjimup

Sample No.	Month	EC $\mu\text{S}\cdot\text{cm}^{-1}$	%			
			Ca	Mg	K	Na
D5	Jan.	1 395	8	23	1	68
	Feb.	1 856	8	24	1	67
	Mar.					
	Apr.					
	May	1 578	6	19	1	74
	June	1 048	6	21	1	72
	July	929	6	20	1	73
	Aug.					
	Sept.					
	Oct.	728	6	21	1	72
	Nov.	777	7	21	1	71
	Dec.	892	7	21	1	71
Mean			6·8	21·2	1·0	71·0
D2	Jan.	548	6	19	1	74
	Feb.	431	7	18	2	73
	Mar.	436	8	20	2	70
	Apr.	605	9	21	1	69
	May					
	June					
	July					
	Aug.					
	Sept.	180	9	20	1	70
	Oct.	643	9	22	1	68
	Nov.	656	9	22	1	68
	Dec.	651	8	20	1	71
Mean			8·1	20·2	1·2	70·5
S21	Jan.	711	7	19	2	72
	Feb.	937	10	21	2	67
	Mar.					
	Apr.					
	May	1 252	9	22	1	68
	June	578	8	27	1	64
	July	599	6	25	1	68
	Aug.	302	4	18	2	76
	Sept.					
	Oct.	458	5	19	1	75
	Nov.	544	6	20	1	73
	Dec.	560	5	19	1	75
Mean			6·7	21·1	1·3	70·9

Mundaring

Sample No.	Month	EC $\mu\text{S}\cdot\text{cm}^{-1}$	%			
			Ca	Mg	K	Na
57	Jan.					
	Feb.					
	Mar.					
	Apr.					
	May					
	June	579	5	21	1	73
	July	639	5	20	1	74
	Aug.	344	5	18	1	76
	Sept.	511	4	19	1	76
	Oct.	567	5	20	1	74
	Nov.	676	5	21	1	73
	Dec.	1 008	5	22	1	72
Mean			4·9	20·1	1·0	74·0
120	Jan.					
	Feb.					
	Mar.					
	Apr.					
	May					
	June	2 406	6	23	1	70
	July	1 479	5	20	1	74
	Aug.	401	6	20	2	72
	Sept.	882	7	16	1	76
	Oct.	1 136	5	21	1	73
	Nov.	1 765	6	22	1	71
	Dec.	2 425	7	24	1	68
Mean			6·0	20·9	1·1	72·0
132	Jan.					
	Feb.					
	Mar.					
	Apr.					
	May	5 470	9	28	<1	63
	June	3 758	8	27	<1	65
	July	3 131	8	25	<1	67
	Aug.	552	8	23	1	68
	Sept.	1 340	7	24	1	68
	Oct.	2 107	8	25	1	66
	Nov.	2 175	8	26	<1	66
	Dec.	3 781	9	26	<1	65
Mean			7·9	25·4	0·7	66·0

Because there were unequal numbers of observations from each stream a simple one-way classification analysis of variance was performed for each region. The summarised analyses of variance data are shown in Table 18, and these results indicate that some of the differences between streams within a region are statistically significant.

TABLE 18

CATIONIC COMPOSITION

One-way classification, analysis of variance F values

Region	Element				
	df	Ca	Mg	K	Na
Busselton	2 & 22	1·80 NS	0·60 NS	0·73 NS	0·78 NS
Dwellingup	2 & 33	10·66 ***	0·36 NS	15·64 ***	3·55 *
Manjimup	2 & 22	2·61 NS	0·49 NS	1·57 NS	0·09 NS
Mundaring	2 & 19	51·09 ***	17·59 ***	5·89 *	32·93 ***

In addition, the mean percentage values for these streams were transformed to angular values (Fisher and Yates, 1963; Snedecor and Cochran, 1973), and a more detailed analysis of variance carried out (Table 17). In this analysis the only significant interaction was between the different regions and the elements present in the waters.

TABLE 19

CATION COMPOSITION

Angular transformation of mean percentage values

Analysis of variance

Source	df	SS	MS	VR	
Regions (1)	3	0·428 223	0·142 741	0·07	NS
Streams (2)	2	0·151 850	0·075 925	0·04	NS
Elements (3) (a)	3	18 788·78	6 262·927	3 236·94	***
1 x 2	6	0·739 483	0·123 247	0·06	NS
1 x 3	9	58·693 34	6·521 482	3·37	*
2 x 3	6	4·990 150	0·831 692	0·43	NS
1 x 2 x 3	18	34·826 98	1·934 832	....	....
Total	47	18 888·61	....	....	....

(a) Ca, Mg, K and Na.

(6) **Anionic composition of waters**

The three major anions present in the waters were chloride, bicarbonate and sulphate. A series of samples covering the EC range of 220 to 3100 μS·cm^{-1} showed the following mean composition:

chloride—86%
bicarbonate—9%
sulphate—5%.

As all streams were predominantly chloride waters the estimation of the minor anionic constituents was restricted to several samples from each area, and in the majority of samples chloride was the only anion determined.

From the analytical data available, the proportion of sulphate ions appeared relatively constant throughout the regions, and any variation in anionic composition was due to the chloride and bicarbonate ions. Over the whole sampling period chloride varied from 80% to 95%, and there was a tendency for the proportion of bicarbonate to reach a maximum during the winter months. An example of the seasonal variations of these anions is shown in Table 20.

TABLE 20
SEASONAL VARIATION IN ANIONIC COMPOSITION
% composition

Month	Busselton B1		Dwellingup BD14		Manjimup S21		Mundaring 120	
	Cl	HCO_3	Cl	HCO_3	Cl	HCO_3	Cl	HCO_3
Jan.	87	7	87	10	82	14	....	....
Feb.	....	....	82	12	84	13	....	....
March	....	....	86	10	....	....	....	....
Apr.	....	....	86	9	....	....	....	....
May	....	....	91	9	89	7	....	....
June	95	3	90	8	90	5	96	2
July	83	12	85	11	....	....	85	10
Aug.	82	14	84	10	87	11	85	13
Sept.	81	14	87	11	....	....	88	9
Oct.	89	6	89	6	89	7	91	4
Nov.	88	6	83	13	90	4	95	3
Dec.	82	12	86	9	90	8	95	3
Mean	85·9	9·2	86·3	9·8	87·6	8·6	90·7	6·3

The anionic concentration followed a similar pattern to that of the cations when related to the seasonal variation in EC values, with minimum values being recorded during the cool, wet winter months, and maximum values during the late spring and summer months when base flow water becomes the dominant source of the stream water. The chloride values observed covered the range 1-200 me·l^{-1}.

DISCUSSION

The principal factor influencing the chemical composition of the forest streams is the nature of the soil through which the rain water percolates prior to entering the stream. The broad soil pattern throughout the area consists of Darling Range laterites and small areas of younger soils formed from fresh rock and asociated young deposits (Mulcahy, 1973).

Evidently there must be considerable variation in the concentration of soluble salts in the various subsoils to cause the wide range of EC values encountered in the study. However, despite these variations, the ionic composition of the streams was virtually constant throughout the four regions. It is considered that this uniformity in the waters is a reflection of the uniformity of the deeply weathered subsoil profiles, where the dominant exchangeable cations are magnesium and sodium, and any subterranean water tables tend to show similar ionic proportions to the surface streams.

The ionic composition of the waters is markedly different from that reported in other parts of the world, e.g. Eriksson (1929) showed that Swedish river waters draining an area of soils derived from silicate rocks of magmatic origin contained calcium as the major cation. In a study of the composition of inland waters Clarke (1924) determined that the mean ionic ratios (calculated from chemical equivalents) of the four major cations were:

Ca : Mg : K : Na = 1.0 : 0.28 : 0.05 : 0.25

and the anion ratio was:

$Cl : SO_4 = 1.0 : 1.58$.

The corresponding ratios for the Western Australian forest streams were:

Ca : Mg : K : Na = 1.0 : 3.63 : 0.25 : 12.67

$Cl : SO_4 = 1.0 : 0.04$.

These data would tend to indicate that ions derived from the weathering of primary rock material are of little significance in determining the composition of the stream waters.

Another important source of ions is via the accession from rainfall, and over the forest region this is derived from the evaporation of sea water from the Indian and Southern Oceans. The ionic ratios for sea water (Goldschmidt, 1958) and rain water at Dwellingup (Hingston, 1958) are compared with the stream waters in Table 21.

TABLE 21

IONIC RATIOS OF SEA, RAIN AND FOREST STREAM WATER

(Ratios calculated from chemical equivalents)

Water source	Ca	:	Mg	:	K	:	Na	Cl	:	SO_4
Sea water	1·0	:	5·36	:	0·49	:	23·10	1·0	:	0·10
Rain water (Dwellingup)	1·0		3·00		0·50		11·50	1·0		0·15
Forest streams (all regions)	1·0		3·63		0·25		12·67	1·0		0·04

The stream water and rain water cationic ratios are similar, with the rain showing a slightly lower magnesium and sodium and a higher potassium ratio than the streams. For the anionic ratio, the proportion of sulphate is much lower in the forest streams. The higher magnesium and sodium ratios in the streams are probably a reflection of the exchange complex in the subsoils where these elements are the dominant cations. The lower potassium and sulphate ratios could be due to the forest crop "filtering off" these two nutrients as soon as they enter into the hydrological cycle.

ACKNOWLEDGEMENTS

The author gratefully acknowledges the assistance of Mr. A. Selkirk who was responsible for the collection of Mundaring water samples, and the help of Research Staff at Busselton, Dwellingup and Manjimup in collecting samples from these three regions.

Considerable thanks are also due to Mrs. C. Y. Goodlet who was associated with the bulk of the analytical work involved in the project.

REFERENCES

APHA (1969). Standard Methods for the Examination of Water and Wastewater. (12th edn, American Public Health Association, New York.)

Australian Water Resources Council (1969). Quality Aspects of Farm Water Supplies. Dep. of National Development, Canberra.

Bond, R. D. (1955). Determination of low concentrations of sulphate using barium chloride and ethylenediaminetetraacetic acid (EDTA). Chem. & Ind., 941-942.

Clarke, F. W. (1924). The Data of Geochemistry. U.S. Geol. Surv. Bull. 770. 5th edn.

Cochran, W. G. (1972). Sampling Techniques (Charles E. Tuttle, Tokyo).

Eriksson, J. V. (1929). Medd. Stat. Meteorolog.-hydrogr. Anst. 5, No. 3, (quoted by Goldschmidt, 1958).

Fisher, R. A. and Yates, F. (1963). Statistical Tables 6th edn, Oliver & Boyd, Edinburgh).

Goldschmidt, V. M. (1958). Geochemistry. (1st edn, revised Oxford University Press).

Hart, B. T. (1974). A compilation of Australian water quality criteria. Aust. Wat. Resour. Coun. Tech. Pap. No. 7 (Aust. Govt. Publishing Service, Canberra).

Hingston, F. J. (1958). The major ions in Western Australian rainwaters. C.S.I.R.O. Div. Soils, Divisional Report 1/58.

La Sala, A. M. Jr. (1967). New approaches to water resource investigation in upstate New York. Ground Water 5, 6-11.

Mulcahy, M. J. (1973). Landforms and soils of southwestern Australia. J. Roy. Soc. W. Aust. 56, 16-22.

Murphy, J. and Riley, J. P. (1962). A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta 27, 31-36.

Pinder, G. F. and Jones, J. F. (1969). Determination of ground water component of peak discharge from the chemistry of total runoff. Wat. Resour. Res. 5, 438-445.

Piper, C. S. (1947). Soil and Plant Analysis. (Interscience Publishers, New York).

Piper, C. S. and Lewis, D. G. (1951). The determination of nitrate nitrogen by the xylenol method with particular reference to soils. Report, Waite Agricultural Research Institute, Adelaide.

Public Works Department of Western Australia (1972). Streamflow records of Western Australia, 1939 to 1970. 2 vols.

Ramirez-Munoz, J. (1974). The determination of nitrate in waters at low ppm levels by automatic discrete sample analysis. Anal. Chim. Acta 72, 437-442.

Richards, L. A. (ed.) (1969). Diagnosis and improvement of saline and alkali soils. Agriculture Handbook No. 60. U.S. Dep. Agric.

Snedecor, G. W. and Cochran, W. C. (1973). Statistical Methods (6th edn, Iowa State University Press).

Varian Techtron (1972). Analytical Methods for Flame Spectroscopy.

Vogel, A. I. (1968). A text-book of Quantitative Inorganic Analysis. (3rd edn, Longmans, London.)

Welcher, F. J. (1958). The Analytical Uses of Ethylenediaminetetraacetic Acid. (D. Van Nostrand, New York.)

Williams, E. J. (1959). Regression Analysis. (John Wiley, New York.)

102395/1/76—1M

WILLIAM C. BROWN, Government Printer, Western Australia