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Stream Water Quality of Forest Catchments in the Cotter Valley, ACT

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SUMMARY Water samples were collected from 1974 to 1977 at 19 sampling stations in the lower Cotter Valley. These stations cover a considerable range of altitude, rainfall and forest type. The geology and soils of the area are diverse. Records of stream discharge were available at 16 sites on gauged catchments. Most samples were obtained at regular weekly intervals; additional samples were taken at 6-hourly intervals for a few selected storm periods on 4 catchments. Water samples were analysed for soluble calcium, magnesium, sodium, potassium and chloride, and for total iron, pH and electrical conductivity. Water quality and composition depended more on geological and soil properties than on vegetation type. Mean electrolyte content was lowest on metamorphosed sedimetary rocks, it was highest in streams draining catchments on Paddy's river volcanics. On sedimentary catchments the electrolyte content of stream water tended to increase with decreasing altitude and rainfall. Stream water from undisturbed pine plantations had a composition and electrolyte content that was comparable to that of water draining geologically similar adjacent catchments supporting native vegetation. Increased soluble potassium and total iron transport was noted on catchments where pine had been harvested during the sampling period. Ion concentrations varied little with discharge on permeable catchments, whose streams mainly receive groundwater flow, but varied with discharge on the less permeable catchments, where substantial amounts of flow originate from shallow surface soil layers and from overland flow over saturated areas. On these less permeable catchments concentrations of calcium, magnesium, sodium and chloride, and electrical conductivity decreased at high flow, but reverse trends were observed for potassium and total iron.

1 INTRODUCTION

Until recently, runoff from the Cotter Valley provided the only water supply for Canberra. Although the area has mainly remained under native forest for runoff protection, substantial areas in the lower part of the valley had been progressively planted since the 1920s to radiata pine. Subsequent management and harvesting of some plantations caused concern about water quality. Additionally, concern was felt about the possible effects of intensified management, and of wild fires, in native forests on both runoff and water quality.

Therefore, several instrumented catchments were established between 1964 and 1972, to obtain basic data on water chemistry as well as to ultimately ascertain the effects of various management practices. Some catchments were paired for immediate treatment, on others long-term measurements were made to obtain calibration data before applying treatments. Data on the following water quality parameters were collected between 1974 to the end of 1977: turbidity, soluble calcium, magnesium, sodium, potassium and chloride, pH, electrical conductivity (EC) and total (water soluble and bound to particulate matter) iron.

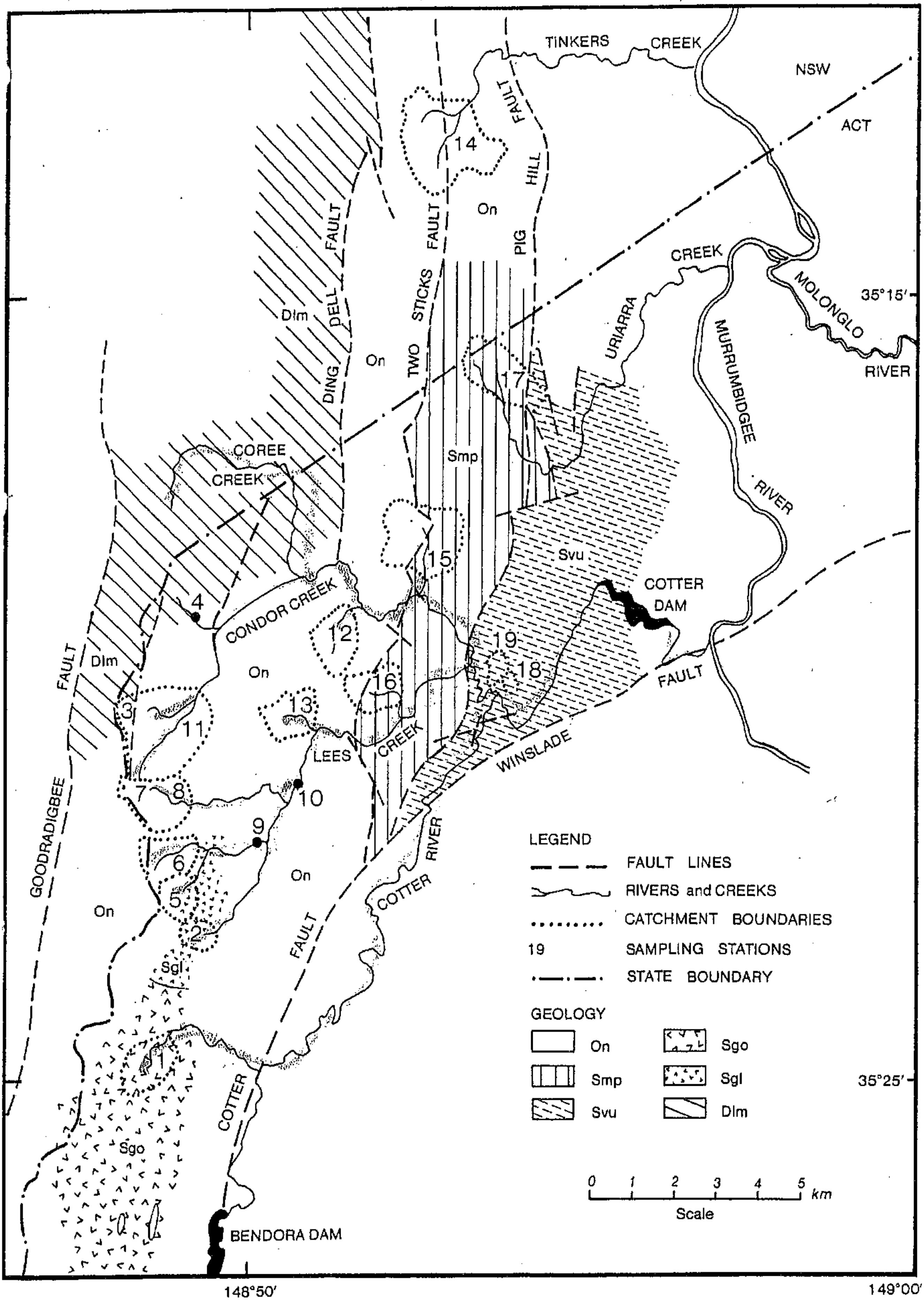
Results of turbidity sampling in this period did not differ from those reported by Thistlethwaite (1970), who reported mainly point source contamination of short duration. Measurements of nitrogen and phosphorus formed a small part of the sampling program. These data are not reported here.

In this paper we document the information obtained on water chemistry, and we attempt to relate the results to the environmental factors of geology, soils and vegetation, and to catchment discharge. Where possible, vegetation management factors will be discussed.

2 THE STUDY AREA

The experimental catchments in the lower Cotter Valley lie at altitudes between 600-1400 m, with mean annual precipitation of 750-1200 mm. Both the geology and soils of the area are diverse. The 19 sampling sites used in this study are located to the west of the Cotter and Murrumbidgee rivers (Map 1). Sites 1-11 are at high elevation in the Brindabella Range, the remainder are at lower elevation towards the valley of each river. Geological detail on Map 1 is derived from sheet 8627 (Brindabella), 1:100 000 Geological Series (Owen and Wyborn, 1979). Sixteen of the sampling sites are also stream gauging sites for experimental catchments, two (3 and 7) are permanent groundwater springs and one (4) is on an ungauged creek. Table I gives further details on geology, sub-soil hydraulic conductivity, catchment size and elevation, rainfall and vegetation type. During the sampling period, annual precipitation exceeded the 15 year means in Table I by over 50% in 1974 and by some 30% in 1975; 1976 and 1977 were slightly below these averages.

Native vegetation alters gradually from mixed dry and wet sclerophyll (major Eucalypt species : *E. dives, pauciflora, dalrympleana, radiata* and *delegatensis*) at higher elevation and rainfall to dry sclerophyll (*E. dives, radiata, maculosa, rossii, macrorhynca*) at lower, drier sites. The only recent management of eucalypt catchments has been a low intensity control burn on Picadilly (Station 8) in March, 1973. Pine plantations are of variable age; management during the sampling period includes clearfelling of Compartment 97 (19) in 1972, and progressive felling of Compartment 99 (18) over the whole sampling period. About 20% of the Blue Range catchment (15) was windthrown in 1974 and progressive but incomplete harvesting took place on this catchment from then onwards. Greens



Map 1 Location of sampling sites in the lower Cotter Valley

TABLE I

SITE DETAILS FOR EACH OF THE SURFACE WATER SAMPLING SITES IN THE COTTER VALLEY, ACT

Nr	Sampling station[1]	Geology[2]	H.C.[3] (mm hr^{-1})	Catchment area (km^2)	Elevation (m)	Rain[4] (mm yr^{-1})	Vegetation type[5]
1	Bushrangers	Sgo	1.4	0.93	980-1260	1010	DWS
2	Pago	Sgl	5.8	0.33	1160-1360	1090	DWS
3	Two Sticks	Dlm	-	-	1150	-	DWS
4	Condor Ck	Dlm	-	-	1000	-	DWS
5	Bulls Head	On (Sgl)	21.0(5.7)	0.74	1140-1360	1090	DWS
6	Ferny	On	14.0	1.02	1120-1330	1060	DWS
7	Picadilly	On	-	-	1220	-	DWS
8	Picadilly	On	23.0	1.32	1060-1240	1040	DWS
9	Warks	On	-	3.70	900-1360	1020	DWS
10	Lees	On (Sgl)	-	5.00	820-1360	990	DWS
11	Sunshine	On (Dlm)	-	4.20	850-1300	990	DWS
12	Marshalls	On	-	1.08	720-1050	890	DS
13	Howells	On	8.3	1.10	780-1040	940	Pine (1960)
14	Blundells	On	-	4.20	700- 950	890	DS
15	Blue Range	On, Smp	5.2,0.6	2.60	670- 940	890	Pine (1939)
16	Greens	Smp (On)	1.4(6.6)	0.93	700- 980	890	Pine (1951)
17	Uriarra	Smp (Svu)	0.2	1.79	620- 860	840	G,DS
18	Cpt 99	Svu	0.5	0.11	580- 670	760	Pine (1934)
19	Cpt 97	Svu	0.5	0.28	580- 670	760	Pine (1934)

[1] All sampling stations at catchment weirs, except 3 and 7 (permanent springs), and 4 (ungauged Creek).

[2] Map notations from Owen and Wyborn (1979). Sgo = Bendora granodiorite, Sgl = unnamed leucogranite, Dlm = Devonian volcanics (Mountain Creek member), On = Ordovician metamorphosed sediments (Nungar Beds), Smp = Silurian volcanics (Paddy's River member), Svu = Silurian volcanics (Uriarra Crossing member). Minor components in brackets.

[3] Mean hydraulic conductivity of sub-soil (700-100 cm depth), -: no data

[4] Approximate means over 15 year period: 1962-1977

[5] DWS = mixed dry and wet sclerophyll, DS = dry sclerophyll, G = pasture, (1960) etc. = planting dates; for subsequent management details see text

(16) was thinned from late 1976 to early 1977. No significant management was imposed on Howells (13).

The distribution of soil groups is largely determined by geology (Talsma and Hallam, 1980). Soils on granodiorite (Sgo) are generally massive red and yellow earths of modest permeability (Table I). On sedimentary deposits (On) major soil types are krasnozems and friable red earths. Both are permeable, especially the krasnozems, which are predominant at high elevation. Soils on the volcanic formations Smp and Svu are massive yellow earths on steeper slopes; these grade progressively into red and yellow podzolics toward valley bottoms. The yellow earths and red podzolics are moderately to slowly permeable but yellow podzolics, the dominant soils at Uriarra (17), are nearly impermeable in the subsoil (Table I). Talsma and Hallam (1980) list details on soil profile hydraulic conductivity for four catchments (1,5,8 and 17 in Table I) and briefly discuss differences in hydrological response to mean profile hydraulic conductivity characteristics of these catchments.

Percentages of Ca, Mg, Na, K and Fe in fresh rock samples are given in Table II. Although these mean data, especially those from limited sample numbers, may not adequately represent the average on individual catchments, we note that Ca is more abundant relative to Mg, in the granodiorite (Sgo) and Devonian volcanics (Dlm) than in the Silurian volcanics (Smp, Svu) and sedimentary rocks (On). The Ordovician sediments in this region are characterised by low Ca and Na (R. Evans, personal communication).

TABLE II

ROCK COMPOSITION OF MAJOR GEOLOGICAL UNITS

Geology[1]	Cation content (% of rock)					Samples
	CaO	MgO	Na_2O	K_2O	FeO Fe_2O_3	
Sgo	2.23	1.49	2.73	3.16	3.60	2
Dlm	2.09	1.10	3.57	4.45	3.28	15
On	0.26	2.12	0.66	3.62	na	24
Smp	1.66	2.26	3.21	3.30	4.24	6
Svu	0.97	1.25	4.18	3.80	2.38	6

[1] Dlm, Sgo, Smp and Svu samples from Owen and Wyborn (1979). On-formation data from regional samples in the Southern Tablelands (R. Evans, personal communication).

na = data not available

3 EXPERIMENTAL DETAIL

3.1 Field Sample Collection

During the four year sampling period, water for chemical analysis was collected routinely at weekly intervals, with some additional collection at short intervals during 2 or 3 selected storm periods on several catchments. This has led to a slight bias of sample numbers collected at high flow especially on ephemeral streams (in particular stations 16-19). In general however, for this area with rather infrequent large storm events, sampling occurred mainly at low and intermediate flow. At the gauged catchments sample collection, in 2.25 ℓ plastic bottles, took place just upstream from the stilling ponds. Gauging sites consist of 90 or 120° sharp-crested V-notch weirs, equipped with Leupold-Stevens A-35 recorders. In 1977 automatic samplers collected 6-hourly samples across storm hydrographs at stations 6, 8, 15 and 17.

3.2 Laboratory Analyses

From 1974-1976 samples were taken to the laboratory on the collection day, and all analyses were completed within four days. During 1977 samples were frozen and stored for processing in large batches.

Sodium and potassium were determined on the untreated samples by atomic absorption spectroscopy, using a propane/air flame. Iron was determined by atomic absorption spectroscopy using an acetylene/air flame after digestion of the unfiltered sample with HCl. Strontium chloride was added to samples for calcium and magnesium before analysis by atomic absorption spectroscopy using an acetylene/air flame.

Before 1977, chloride was determined by conductimetric titration with $AgNO_3$ as described in Anon. (1971). During 1977 chloride was determined colourimetrically by auto-analysis using Technicon Industrial Method 99-70W. Electrical conductivity was measured at 20°C with a meter standardised to the conductivity of a standard solution of 0.005 M NaCl solution, equivalent to 56.2 $\mu S\ cm^{-1}$.

4 ANALYSIS OF EXPERIMENTAL DATA

4.1 Data Presentation

Space limitation prevents presentation of many details of analysis of the broad sampling program. Here, we present selected results under two headings, which permits the establishment of general trends.

Firstly using the means of all data, water quality and composition is related to geology and soils. Secondly, we explore factors responsible for differences in discharge - water quality relationships amongst the various catchments. No consideration is given to other reasons such as hysteresis and seasonal variability for data scatter, nor possible functional relationships between quality and discharge. These aspects are documented by Lane (1975).

4.2 Water Quality and Composition in Relation to Geology and Soils

Data on streamwater quality, in terms of mean values of pH, EC, cations, chloride and total iron at all sampling stations are given in Table III. The data of Table III are summarised in Table IV for each geological subdivision, in terms of major cation composition and ion ratios.

TABLE III

MEAN pH, EC, SOLUBLE Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^{-1}, AND TOTAL Fe (as Fe^{2+}) AT WATER SAMPLING SITES. MEANS OF BETWEEN 100-200 SAMPLES

Station	pH	EC (μScm^{-1})	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	Fe^{2+}
			(meq m^{-3})					
1	7.1	55.1	127	98	274	38	69	17
2	6.6	23.6	50	49	112	16	45	10
3	6.2	34.5	68	50	170	39	76	45
4	6.6	24.8	67	35	97	29	44	5
5	6.6	17.9	22	50	91	9	41	10
6	6.6	23.8	33	80	97	10	45	8
7	5.6	18.2	15	66	116	8	46	6
8	6.1	21.5	28	37	79	8	44	5
9	6.8	30.2	41	83	155	13	59	8
10	6.9	39.6	55	123	179	16	72	12
11	6.8	41.5	55	147	170	21	66	8
12	7.0	59.7	32	226	270	27	115	43
13	7.0	78.1	83	285	317	24	245	10
14	6.9	72.9	49	322	272	35	155	25
15	7.0	81.9	111	280	338	53	206	65
16	7.2	152.7	520	483	484	58	194	114
17	7.0	152.0	446	551	460	57	142	17
18	6.6	44.5	78	125	190	61	114	198
19	6.7	50.0	81	138	214	79	119	157

TABLE IV

CATION COMPOSITION (PER CENT OF MAJOR CATIONS) AND ION RATIOS IN SURFACE WATERS. MEAN DATA FOR GEOLOGICAL SUB-DIVISIONS. DATA DERIVED FROM TABLE III

Stations	Geology	Ca^{2+} (%)	Mg^{2+} (%)	Na^+ (%)	K^+ (%)	$\frac{Ca}{Mg}$	$\frac{Ca + Mg}{Na + K}$	$\frac{Na}{Cl}$
1,2	Granites (Sgo, Sgl)	23	20	50	7	1.16	0.75	3.21
3,4	Devonian Volc. (Dlm)	25	15	47	13	1.62	0.70	2.22
5-15	Meta sediments (On)	12	35	48	5	0.37	0.89	2.12
16,17	Silurian Volc. (Smp)	34	34	30	4	0.94	1.89	2.87
18,19	Silurian Volc. (Svu)	16	28	42	14	0.60	0.78	1.73

We note (Table III) that the electrolyte content, expressed as EC, is lowest (about twice that of local rainwater) for waters from the high altitude stations (5-8) on metamorphosed sedimentary rocks. Values of EC on this geological formation gradually increase with decreasing altitude and rainfall. Streams and springs at high altitude on granite (1,2) and Mountain Creek volcanics (3,4) have slightly higher values of EC, than on meta sedimentary rocks at this altitude. Highest mean values of EC occur in streams draining catchments (16,17) on Paddy's river volcanics (Smp). These catchments have a large proportion of fine textured soils. In contrast, catchments (18,19) on Uriarra volcanics (Svu), with much shallower and coarser textured soils, have relatively low values of EC. Mean pH values are lowest where the calcium content in streamwater (with respect to other cations) is low, see e.g. station 7.

Calcium to magnesium ratios of streamwater on Dlm, Sgo, Sgl, On, Smp and Svu formations (Table IV) are similar to those of the parent rocks (Table II), irrespective of vegetation type or management. This is particularly evident for sedimentary catchments, but distinct differences in Ca:Mg, and (Ca+Mg):(Na+K) exist within small distances in On formations; compare for example spring water at Picadilly (7) with streamwater collected at the gauging station (8) some distance below, which indicates the variable lithology of this formation.

The sodium content in streamwater is typically between 40-50% of the major cations, except for the Smp formation. Potassium is low in nearly all catchment streams on the On and Smp formations (one exception being Blue Range (15), where K is 7%) but is higher on the Dlm, Sgo, Sgl and Svu formations. Soils on granitics (Sgo, Sgl) contain mica and have relatively high exchangeable K (12%). Soils on Uriarra volcanics, (Svu) have exchangeable K (5%) equal to that of soils derived from On and Smp deposits. Therefore the higher percentage of K in streamwater at sampling stations 18 and 19 (Svu) is unlikely to be due to soil factors. We discuss this aspect later.

Na:Cl is high, 2.5-4.0, on the granites (1,2) and Paddy's River volcanics (16,17), compared with all other geological formations where Na:Cl is about 2. The relation between Cl and EC is therefore poor. The relationship between the sum of major cations (Ca, Mg, Na, K) and EC however, is linear and highly significant: $EC = 0.099\ (\Sigma cat)_{1} + 2.33$ ($r= +0.998$, $n= 19$), where EC is in $\mu S\ cm^{-1}$ and $\Sigma(cat)$ is in $me\ m^{-3}$.

Total iron, expressed as Fe^{2+}, is generally low and less than 5% of the total major cations. Exceptions are station 3 (14% of major cations) where particulate matter was often high in summer, 12 (8%) which receives occasional runoff from subsoil material exposed by a major road near the weir, and 15 (8%), 16 (7.5%), 18 (44%) and 19 (31%).

4.3 Water Quality - Stream Discharge Relationships

Examples of water quality-discharge trends found in this study are shown in Fig. 1 for four 6-hourly sampling periods at stations 6 (Ferny), 8 (Picadilly), 15 (Blue Range) and 17 (Uriarra). For clarity data plots are for Ca, Na, K and Cl only; these are plotted together with hourly rain intensities and hydrographs resulting from these storms.

The hydrographs at the permeable Ferny and Picadilly catchments (Table I) indicate predominant (Ferny) and complete (Picadilly) groundwater flow. Cation and anion concentrations vary very little with stream discharge. In contrast, hydrographs from the less permeable Blue Range catchment and the nearly impermeable Uriarra catchment (Table I) exhibit sharp peaks associated with rain intensities frequently in excess of sub-soil hydraulic conductivities (Talsma and Hallam, 1980). At Blue Range Na and Cl concentrations decrease markedly with increasing discharge; Ca decreases and K increases less strongly with increasing discharge (for comparison with Ferny and Picadilly note the difference in concentration scales). At Uriarra, Na and Ca depend strongly on discharge, Cl shows no relation during this storm (although it often did in others) and K again increases with discharge.

Relationships between electrolyte content (EC) and instantaneous discharge (Q), plotted as EC versus ℓnQ, are shown in Fig. 2 for 8 sampling stations. For 2 of these catchments, Picadilly (8) and Blue Range (15), relationships between discharge, Q, and major cations, iron and chloride, are shown in Figs 3a and 3b. The data of Figs. 2 and 3 are based on the results of the regular weekly sampling only.

The EC changes little with Q at the permeable catchments (Table I) Ferny (6), Picadilly (8), Howells (13) (Fig. 2), Bulls Head (5) and Pago (2) (data not shown), moderately for the less permeable catchments Bushrangers (1), (Fig. 2), Marshalls (12) and Blundells (14) (data not shown), and more strongly for the slowly permeable Blue Range (15), Greens (16) Cpt 99 (18) and Uriarra (17) catchments (Fig. 2). The decrease of EC with Q, on all catchments that show this characteristic, is associated with decreasing concentrations of Ca, Mg, Na and Cl (see Fig. 3 for Blue Range). K is a minor component (Table IV) and its concentration did not increase greatly at high discharge. The increasing trend of Fe with Q, as shown in Fig. 3b for Blue Range, is partly due to increased discharge of particulate matter, and so would not affect the EC - Q relationship greatly.

5 DISCUSSION

5.1 Geology and Soil Factors

The strong dependence of water quality and its ionic composition on regional geology and soils has been noted in several other studies (e.g. Walling and Webb 1975; Henderson *et al.* 1978; Geary, 1981) especially for the major cations Ca, Mg and Na, and the anions Cl, SO_4 and HCO_3. The control of geological and soil properties, rather than of vegetation, on water quality and composition prevents detailed comparison of our catchments carrying native vegetation which, with the exception of Howells (13) and part of Blue Range (15), are on metamorphosed sedimentary deposits, with those that were cleared and planted to radiata pine. The latter, with the exception of Uriarra (17), are largely confined to areas underlain by Silurian volcanics (Map 1, Table I). We note however, that water quality on the pine plantation at Howells (13), which was not disturbed during the sampling period, did not differ much from that of the geologically comparable (On) catchments 12 (Marshalls) and 14 (Blundells). Also water quality and composition (except Fe) were very similar at Greens (16) carrying pine, and Uriarra (17) under mixed eucalypt and pasture. These catchments are predominantly on Paddy's river volcanics.

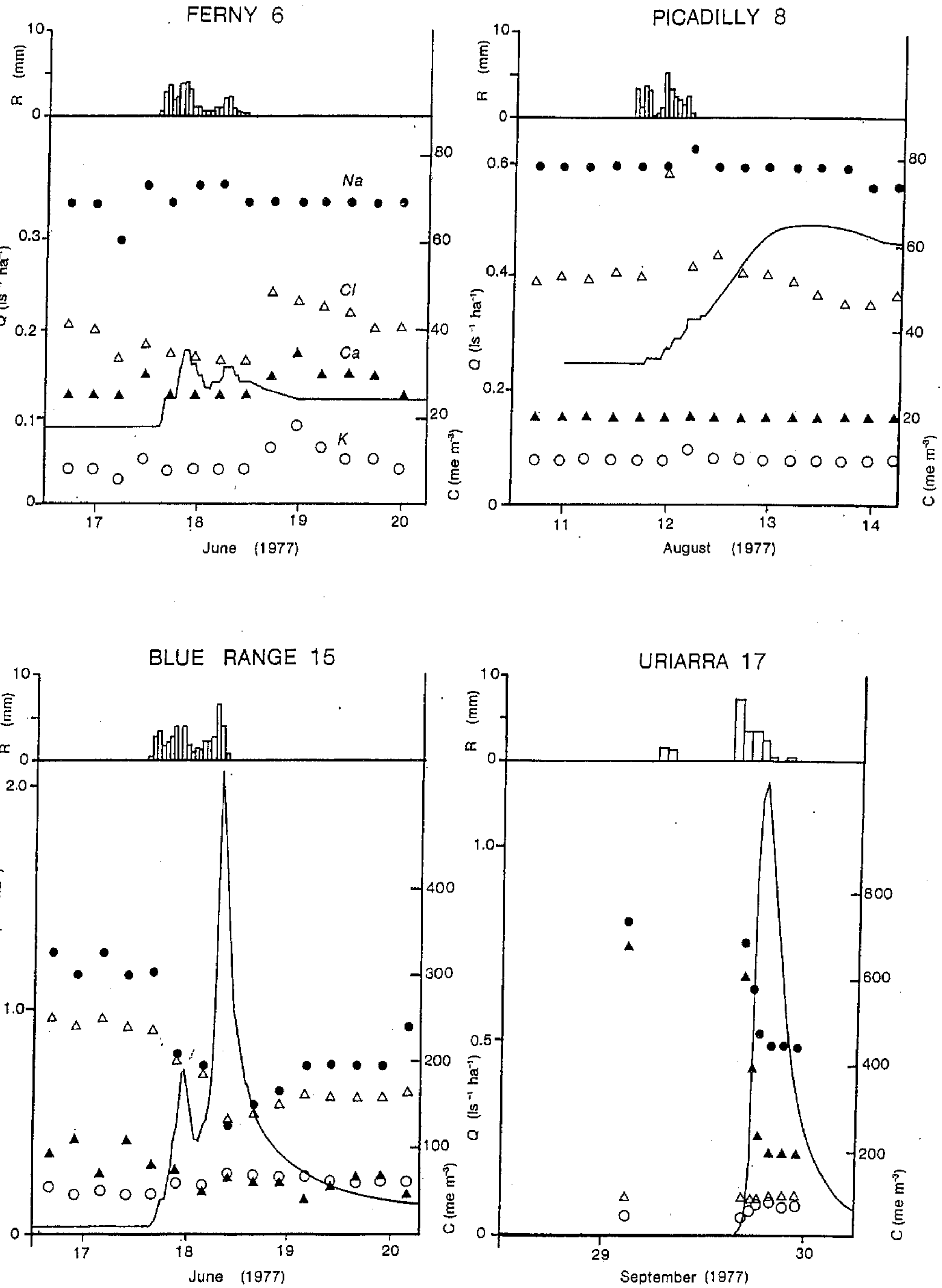


Figure 1 Ion concentrations, C, rain intensities, R, and discharge, Q, during selected storm events on four catchments

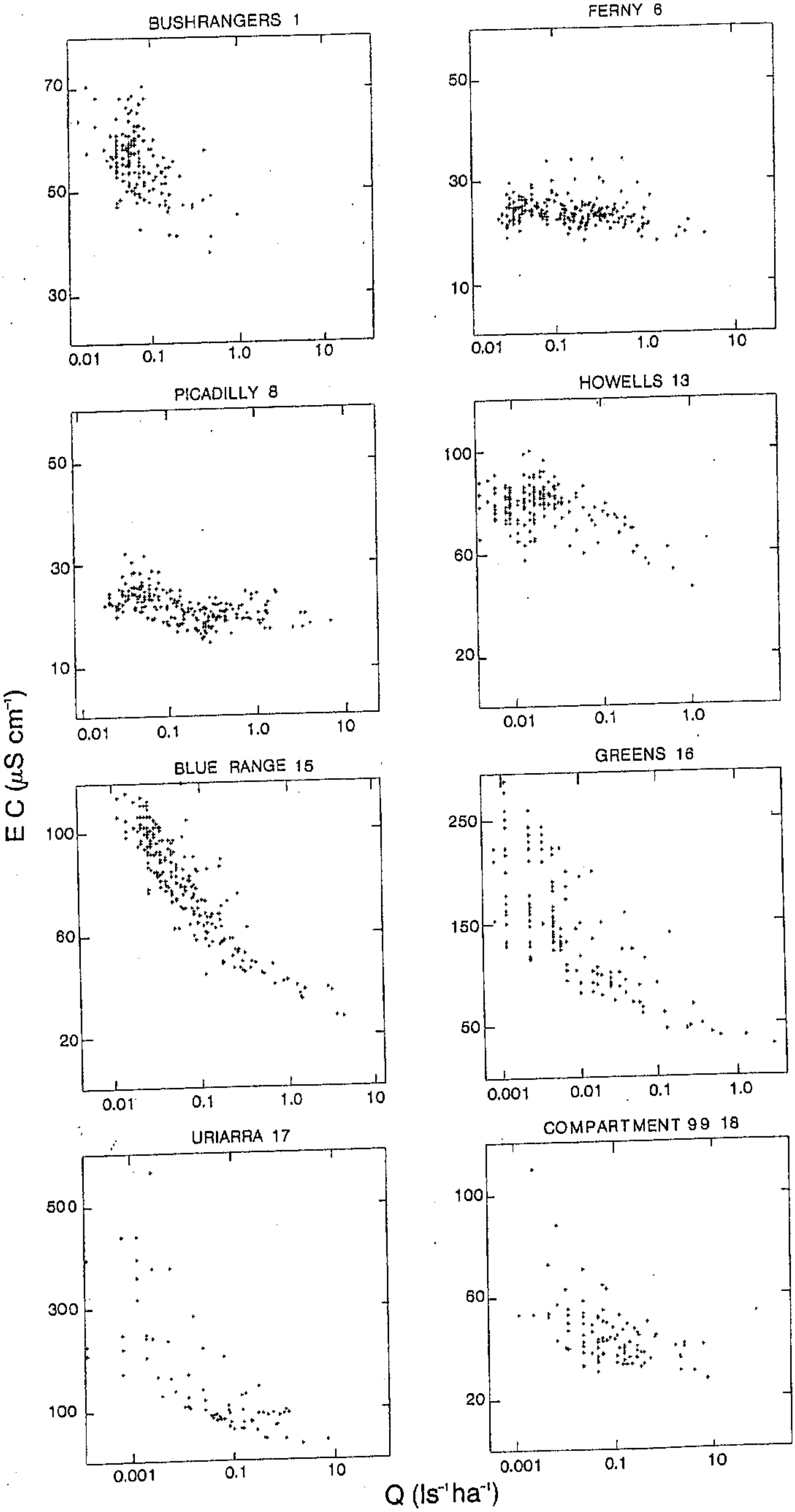


Figure 2 Relationships between electrical conductivity and discharge for eight catchments

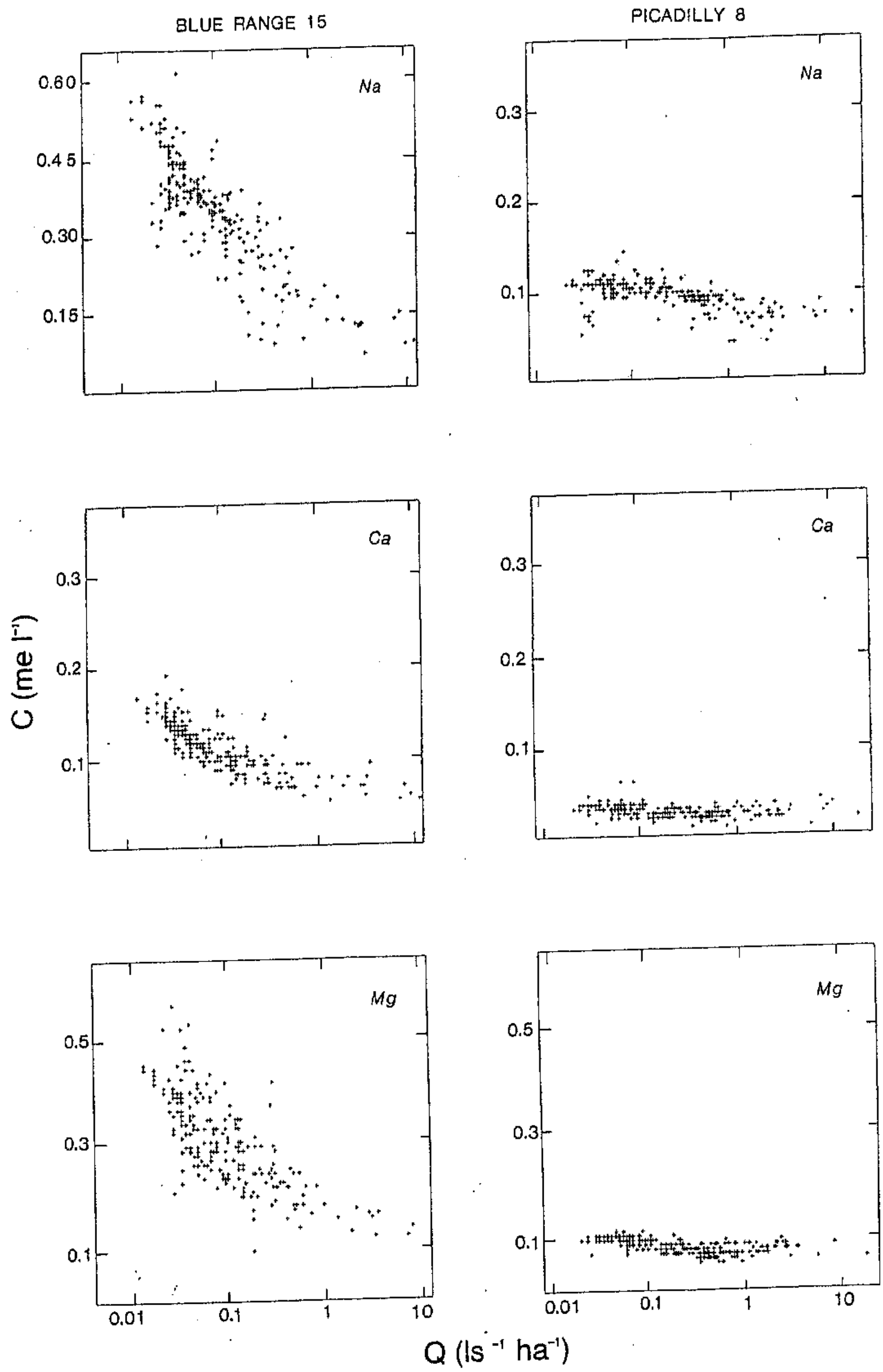


Figure 3a Relationships between discharge, Q, and Na, Ca and Mg concentrations, C, for Blue Range (15) and Picadilly (8)

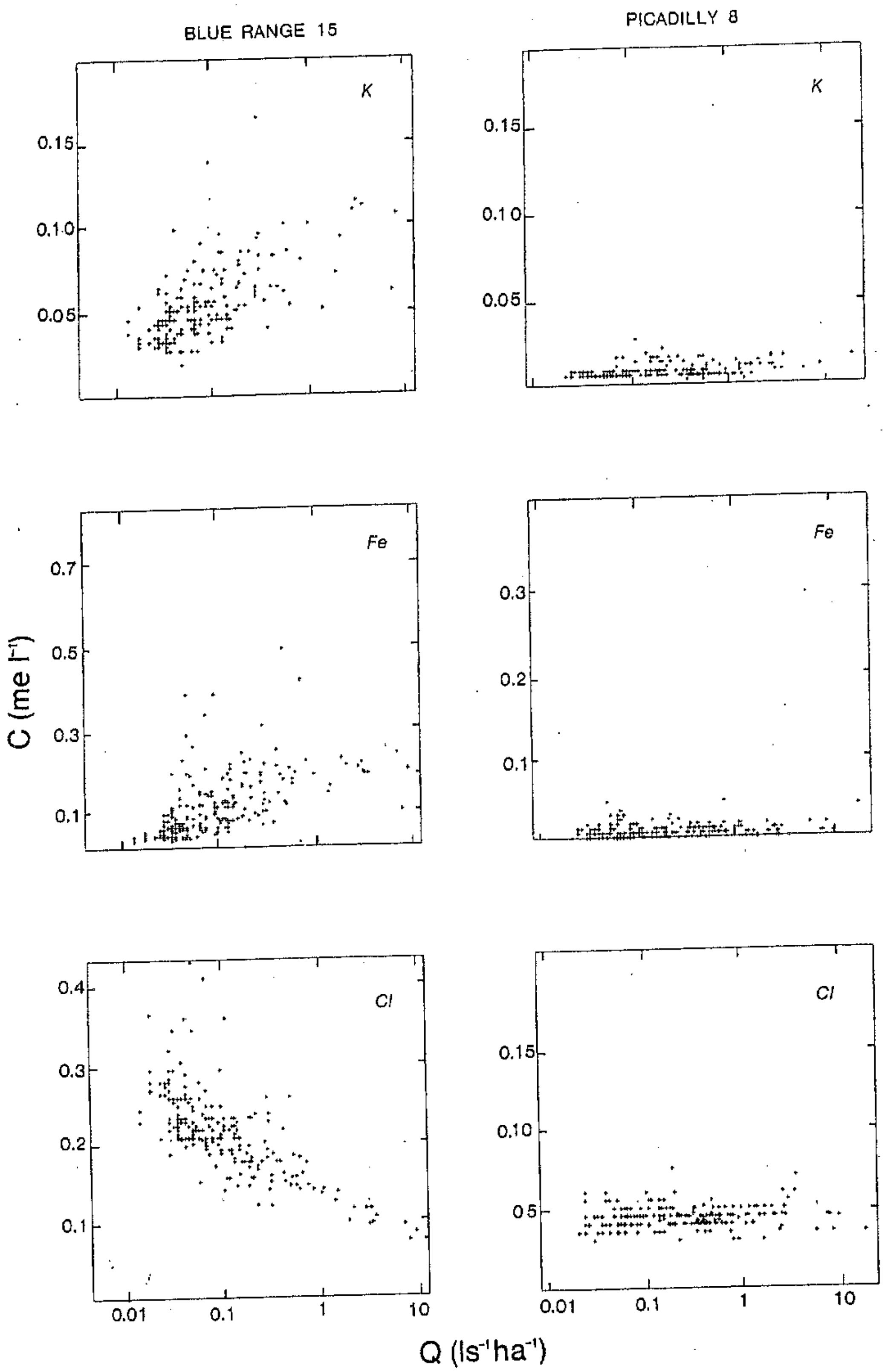


Figure 3b Relationships between discharge, Q, and K, Fe and Cl concentrations, C, for Blue Range (15) and Picadilly (8)

5.2 Effects of Management

We noted in section 4.2 that the relatively high percentages of K at stations 18 and 19, and to a lesser extent on Blue Range (15) (Tables III and IV) could not be attributed to geological or soil differences. Also, total Fe percentages were unusually high on the compartment catchments (18, 19) located on Uriarra Volcanics, which have a rather low iron content in fresh rock samples (Table II). The whole surface area of both these catchments was rather vigorously disturbed, compartment 97 (19) being continually harvested during the sampling period, while Compartment 99 (18) was clearfelled one year before sampling, then windrowed and burnt before replanting. Windthrow damage occurred on Blue Range in 1974, which disturbed some 20% of the catchment surface. We assume that the relatively large concentrations of both K and Fe in streamwater of these three slowly permeable catchments is due to their surface disturbance, which occurred during the sampling period.

The low intensity burn at Picadilly, 9 months before the sampling period, did not affect water quality. This lack of response is not surprising in a catchment that has only deep groundwater runoff with consequent long solute travel times from the soil surface to adjacent streams. In addition, soils on this (and other catchments on metamorphosed sediments) strongly retard both cation and anion transport. Details of these processes are given in Talsma *et al.* (1980) and Talsma (1981).

5.3 Discharge-Water Quality Relationships Discussion.

The differences in water quality-discharge relations (Fig. 3) among catchments are strongly related to differing catchment responses to storm runoff (Fig. 1). The magnitude of catchment sub-soil hydraulic conductivity, with respect to prevailing rain intensities, substantially determines the proportions of overland, quick sub-surface, and deep groundwater flow that contribute to discharge (Bonell and Gilmour, 1978; Talsma and Hallam, 1980; Talsma, 1981). Substantial overland and quick sub-surface flow contributions to discharge apparently dilute the ion concentrations present in the groundwater component of discharge. Exceptions are those ions, e.g. K, which are readily leached from forest canopies and litter, and are thus present in overland flow.

Decreases in concentration with increased discharge of several ion species (often with the exception of K as found here) are also reported by Claridge (1970) for Na and Cl, Turvey (1975), Feller and Kimmins (1979), Lewis and Grant (1979) and Geary (1981). Ion concentrations that are only weakly related to discharge are reported by Flinn *et al.* (1979) and by Likens *et al.* (1977) for the Hubbard Brook results on undisturbed catchments, which might indicate that their catchments are permeable. Examples of increased ion concentrations at high discharge are given by Claridge (1970) for Mg and K, and by Cleaves *et al.* (1970) for EC, Ca, Mg, K and SO_4. The latter authors attribute this partly to ion enrichment in canopy throughfall and stem flow in an acid rain environment.

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