Institute of Hydrology

Centre for Ecology & Hydrology

Natural Environment Research Council

Centre for Ecology and Hydrology

Component Institutes
Institute of Freshwater Ecology
Institute of Hydrology
Institute of Terrestrial Ecology
Institute of Virology & Environmental Microbiology

Natural Environment Research Council

Prediction of Acidification and Recovery on a Landscape Scale

Progress Report 26.9.97

PREDICTION OF ACIDIFICATION AND RECOVERY ON A LANDSCAPE SCALE

PROGRESS REPORT 26.9.97

Introduction

Acid deposition resulting from the release of the oxides of sulphur and nitrogen during the combustion of fossil fuels, has been directly linked with a number of environmental problems. These include the acidification of soils and surface waters, harmful effects on human health, decreased fish stocks, forest dieback, reduced crop yields, corrosion of building materials, and reduced atmospheric visibility. The nature of airborne pollution, and its dispersion by the prevailing winds, ensures that acid deposition is a general problem, and not confined to the source area.

A number of initiatives have been introduced in Europe and North America to reduce acid deposition. This includes the 'tall stacks' policy introduced in the UK in 1952; this led to the pollution being transported further afield, with observations of acidified lakes and loss of fish stocks in Scandinavia being blamed partially on emissions from the UK. This led to the realisation that acidic deposition was a Europe-wide problem requiring international solutions. As a result, the United Nations Economic Commission for Europe established the convention on "Long Range Transboundary Air Pollution" in 1979 to promote the reduction of sulphur and nitrogen emissions across Europe. Since then, a number of attempts at emission control, based on percentage reductions, have been adopted by the EEC countries.

Although these international agreements have been generally successful in, for example, reversing soil and lake acidification in the worst affected areas, it is generally recognised that this approach is not targeting emission reductions to areas where they are most needed. A more rational approach to emission reduction is based on critical loads. A critical load for an ecosystem is defined as a "quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to our present knowledge". Thus, critical loads can be estimated for different parts of an ecosystem and are based on damage to, or loss of, a receptor. The present agreed reductions in sulphur emissions for the European Union, based on the critical loads concept, are embodied in the 1994 Oslo Protocol on Further Reductions of Sulphur Emissions (Second S Protocol). For the UK this involves a 70% reduction by 2005, and 80% by 2010, based on 1980 levels.

Assessing the beneficial effects of such reductions is difficult. Currently, benefits are expressed in terms of whether the critical load for a particular ecosystem is, or is not exceeded. This has disadvantages in that the critical load is an all-or-nothing criterion, whereas ecological damage or change is a matter of degree. Whilst models have been applied to quantify the effects of emissions reduction in UK headwater catchments (Jenkins et al., 1997), studies have not been extended to downstream reaches. These are the areas that may, or may not, support fish populations, dependent on the toxicity of the stream waters.

Study Objective

The objective of the study is to develop a framework for predicting catchment acidification and recovery on a landscape scale. This is done in a number of stages:-

(i) Applying the dynamic hydrochemical model MAGIC to several headwater streams having representative soils and geology in a major catchment area.

(ii) Developing a framework for routing outputs from headwater streams and representative units through a whole catchment.

(iii) Extending the MAGIC model to predict chemical outputs from catchment areas where agricultural calcium carbonate applications form the dominant acid neutralization process.

(iv) Demonstrating and validating the model using available databases.

(v) Assessing the suitability of existing databases and data requirements for landscape modelling and identifying gaps.

The time scale of the study is twelve months beginning April 1997. The study will be concentrated in Welsh catchments where recent and detailed data are available.

Method

The work programme has been split into a number of work packages, many being undertaken simultaneously whilst others depending on the outputs of other packages. The time schedule of the work packages is given in Table 1.

Table 1 Schedule of the work packages

		MONTH '97								'98		
Work Package	A	M	J	J	A	S	O	N	D	J	F	M
1 Data Assessment	X	X	X									
2 Catchment Selection			X									
3 Sub-catchments			X	X								
4 Sites without data			X	X	X	X						
5 Hydrological Modelling			X	X								
6 MAGIC Application					X	X	X					
7 Mixing Model							X	X	X			
8 Landscape System					X	X	X	X	X	X		
9 Validation									X	X	X	X
10 Reporting											X	X

1. Data Assessment

As a prerequisite to catchment selection, a detailed data assessment was undertaken. These datasets included:-

(i)	Streamflow chemistry	-	Welsh Acid Waters Monitoring Sites
		-	Other streamflow quality sites monitored by the Environment Agency
		-	Harmonised Monitoring Streamflow database
(ii)	Streamflow	-	National Water Archive
(iii)	Rainfall	-	UK National Raingauge Archive
(iv)	Rainfall chemistry	-	AEA Technology's National Environmental Technology Center (NETCEN) deposition chemistry database
(v)	Evaporation	-	Meteorological Office Rainfall and Evaporation Calculation System (MORECS)
(vi)	Spatial Datasets	-	Digital Terrain Model (DTM)
		-	Solid Geology
		-	Soils data from the Soil Survey and Land Research Centre at Cranfield University
		-	Hydrology of Soil Types (HOST)
		-	Land use from ITE's Landsat derived classification

2. Catchment Selection

The main criterion for catchment selection was based on the availability of streamflow chemistry from the Welsh Acid Waters Monitoring Sites, as this dataset contains recent and readily available data which can be used to calibrate the MAGIC model. Two surveys have been carried out at these sites - one in 1983/84 and the other in 1994/95 - during which stream samples were collected at monthly intervals and analysed for a number of determinands over a twelve month period. A subsequent analysis of the data suggested that those obtained in the 1983/84 survey were suspect, particularly with regard to pH, and it was decided to concentrate on the 1994/95 data. Figure 1 shows the location of these sampling sites.

When these site locations were superimposed on a map of the hydrometric areas, the catchments containing the most sites were the Teifi (14 sites), the Tywi (11 sites) and, to a lesser extent, the Dyfi (5 sites). Accordingly, it was decided to concentrate on the Teifi and the Tywi, with additional work being done on the Dyfi, should time allow. The locations of the monitoring sites within the Teifi are given in Figure 2, and for the Tywi in Figure 3.

Additional streamflow chemistry data were obtained for the Teifi and the Tywi from the Environment Agency. The original datasets contained over 50 monitoring sites for each catchment, including the Acid Waters Monitoring Sites. The frequency of sampling and the determinands analysed for the additional sites varied a great deal. Sub-sets were therefore chosen; these contained most, if not all, the determinands analysed for the Acid Waters Monitoring Sites, and were sampled at least 6 times a year. The data from these sites cover the period 1976 to 1996 (inc.). Their locations in the Teifi (16 sites) are given in Figure 4, and for the Tywi (36 sites) in Figure 5.

In addition to the above, there is a Harmonized Monitoring streamflow site (Simpson, 1978) in each catchment. For the Tywi, this site is at Nantgaredig, the gauged catchment outlet; for the Teifi, the site is at Llechryd Bridge, a small distance downstream of the gauged catchment outlet. Streamflow chemistry data are available from these two sites at approximately monthly intervals from 1975 onwards.

There are two streamflow gauging stations in the Teifi and seven in the Tywi, their locations are shown in Figures 6 and 7 respectively. Daily flow totals are available from all of these sites for varying periods of time on the National Water Archive (IH, 1993).

Rainfall data were obtained following a search of the rainfall records within the UK National Raingauge Archive (Meteorological office, 1991). The sites chosen were those either within the catchment areas or were located in 10 km squares straddling the boundaries of the catchments. This resulted in 29 sites for the Teifi (Fig. 8) and 56 sites for the Tywi (Fig. 9). The frequencies of observations and the periods of records varied for the various gauges, but sufficient data were available to provide estimates of monthly distributed catchment rainfall from 1975 to 1995.

Rainfall chemistry was accessed from the Acid Deposition Monitoring Network (ADMN) database (Devenish, 1986). At present, this consists of 32 sites across the UK and is administered by AEA Technology's National Environmental Technology Center (NETCEN).

Monthly actual evaporation, based on land use, were obtained from the Meteorological Office Rainfall and Evaporation Calculation System (Thompson et al., 1981). This gives average values over 40 sq. km squares based on meteorological data provided from a number of weather stations. For this particular application, one 40 km square (no.144) was found to cover most of the two catchments.

The digital elevation model (DTM) was obtained by digitizing 1:50,000 Ordnance Survey maps to provide altitudes smoothed to a 10 mm vertical resolution on a 50 m horizontal grid. The Teifi (Figure 10), with an altitude range of 2 m to over 580 m, is not as steep as the Tywi (Figure 11), 3 m to over 830 m, though the main topographic characteristics are similar with flat interfluve areas at the tops of the catchments, followed by steep valley sides leading to a flat main river bed.

The solid geology of the Teifi (Fig. 12) and the Tywi (Fig. 13) is relatively simple, dominated by the Llandovery rocks of Silurian age and the Ashgill and Caradoc series of Ordovician age. Both series are composed of shales, mudstones, silty flags, grits and conglomerates. In addition, these is some old red sandstone of the Devonian series in the valley bottom of the Tywi.

The main source of information concerning soils was obtained from the Soil Survey and Land Research Center at Cranfield University. This included 100 m resolution detailed spatial soil data for the two catchments, and soil attributes - depth, bulk density, cation exchange capacity, porosity, exchangeable cations, and organic carbon - for each series.

Additional soils information was obtained from the Hydrology of Soil Types (HOST) dataset, Boorman et al., (1995). This is based on a 1 km grid square, and mainly relates soil type to drainage characteristics. For the Teifi (Fig. 14), by far the dominant HOST class is 17, covering mineral soils with no impermeable or gleyed layer within 100 cm of the surface. There is more variation within the Tywi (Fig. 15), with 50% of the catchment being covered with class 17, and the remaining 50% split between class 16, covering medium drainage mineral soils with a gleyed layer within 40cm of the surface, and class 15, poorly drained peat soils. Generally, the poorly drained soils occupy the interfluve areas and the medium drained soils the valley bottoms.

The vegetation cover within the two catchments was obtained using the Institute of Terrestrial Ecology's Landsat derived classification (Fuller et al., 1994). This classification, carried out in the late 1980s, used remotely sensed images from the Landsat satellite to classify the whole of the UK into 25 land covers at 25 m spatial resolution. For this application, these 25 classes have been merged to produce 6 'hydrologically significant' classes. The percentage areas of each class for both the Teifi and the Tywi are given in Table 2.

Table 2 Percentage Land Cover for the Teifi and Tywi

Land Cover	Teifi	Tywi
GRASS	54%	46%
MOORLAND	16%	19%
FOREST	19%	27%
ARABLE	4%	3%
URBAN	1%	1%
OPEN WATER	-	-

In addition, information is available on the extent and age of the coniferous plantations within the headwater catchments of the Acid Waters Monitoring Sites.

3. Sub-catchments

The locations and areal extents of the Acid Waters Monitoring Sub-catchments in the Teifi and the Tywi are shown in Figs. 16 and 17, respectively. The grid coordinates and the areas draining to the sampling points are given in Table 3.

Table 3 Locations and size of the Acid Waters Monitoring Sub-catchments

Station No.	Name	Grid Coordinates		Area (ha)
(i) TEIFI				
34408	Meurig	271800	267400	1476.3
89119	Berwyn	269400	259700	1081.8
89120	Groes	269450	260000	1302.3
89121	Brefi	266300	255500	1603.5
89122	Clywedog Uchaf	264350	251550	685.8
89123	Egnant	277000	265500	423.5
89124	Mwyro	276950	265450	476.0
89130	Iar	251000	239400	52.3
89131	Ceiliog	251700	239950	116.5
89132	Ceredig	251850	240150	96.0
89133	Cynhenfod	252500	241500	98.8
89135	Duar	255050	241850	194.0
89136	Llwydcoed	255250	241700	115.8
89138	Wernant Uchaf	256500	242800	38.3
(ii) TYWI				
88111	Llyn Brianne L18	280500	248800	83.3
88116	Tributary of Tywi	278300	246250	25.8
89141	Clawdd	265800	246300	129.5
89142	Cothi Upper	270700	248300	841.5
89143	Tributary of Cothi	271500	246950	148.0
89144	Nant Dar	270300	243800	197.0
89145	Twrch Upper	268500	250350	145.5
89147	Dulais	269950	240000	293.0
89148	Tributary of Cothi	269200	243650	106.8
89149	Annell	267850	240500	390.3
88085	Llyn Brianne L15	282050	249600	73.3

The dominant HOST classes and land use for each of the sub-catchments are given in Table 4. Solid geology is not included, as this is dominated by the Llandovery series; this includes shales, mudstones, silty flags, grits, and conglomerates.

Table 4 **Dominant HOST classes and land use for the Acid Waters headwater catchments**

Station No.	HOST classes		Land Use
(i) TEIFI			
34408	26	Poor drainage	Grassland (59%)/Moorland (22%)
89119	15	Poor drainage	Forest (43%)/Grassland (27%)
89120	17	Freely draining	Grassland (52%)/Moorland (32%)
89121	15	Poor drainage	Grassland (45%)/Moorland (27%)
89122	15	Poor drainage	Forest (40%)/Grassland (29%)
89123	15	Poor drainage	Moorland (48%)/Grassland (41%)
89124	15	Poor drainage	Grassland (60%)/Moorland (34%)
89130	15	Poor drainage	Moorland (88%)
89131	15	Poor drainage	Moorland (56%)/Grassland (37%)
89132	15	Poor drainage	Grassland (51%)/Moorland (45%)
89133	17	Freely draining	Grassland (46%)/Moorland (29%)
89135	17	Freely draining	Forest (66%)/Moorland (23%)
89136	17	Freely draining	Forest (65%)/Moorland (22%)
89138	15	Poor drainage	Moorland (50%)/Grassland (46%)
(ii) TYWI			
88111	15	Poor drainage	Forest (41%)/Moorland (26%)
88116	15	Poor drainage	Grassland (47%)/Forest (20%)
89141	26	Poor drainage	Grassland (45%)/Forest (28%)
89142	29	Poor drainage	Grassland (61%)/Moorland (17%)
89143	15	Poor drainage	Grassland (38%)/Forest (26%)
89144	17	Freely draining	Forest (33%)/Grassland (32%)
89145	15	Poor drainage	Grassland (55%)/Moorland (41%)
89147	17	Freely draining	Forest (35%)/Moorland (30%)
89148	17	Freely draining	Grassland (42%)/Forest (37%)
89149	17	Freely draining	Grassland (40%)/Forest (28%)
88085	15	Poor drainage	Moorland (67%)/Grassland (28%)

In addition, Forest Enterprise 1:10K maps have been digitized to provide information on planting dates, clear felled areas, and second rotation planting within the Acid Waters Monitoring sub-catchments. Percentage areas in 1995 for each of the sub-catchments within the Teifi and Tywi are given in Table 5.

A comparison of the forested areas given by the Landsat derived classification and those given by the Forest Enterprise maps shows some discrepancies, particularly for the Tywi sub-catchments. Most of these can be attributed to forestry practices between the late 1980s, when the Landsat images were recorded, and 1995. Others are more difficult to explain. This suggests that some care is required in applying the Landsat classification for 1995 in unmonitored sub-catchments.

Table 5 Percentage areas of planting and felling for the Acid Waters Monitoring Sub-catchments

Station	First Rotation Planting Schedule						Re-Planting		Felled	Deciduous
	p 85-95	p 75-84	p 65-74	p 55-64	p 45-54	pre 45	<3 years	>3 years		
(i) TEIFI										
34408	-	-	3.5	-	-	-	-	-	-	0.1
89119	-	6.4	9.2	32.1	-	-	2.0	-	-	2.7
89120	-	2.4	6.6	-	-	-	-	-	-	1.1
89121	-	0.3	5.8	18.1	-	-	0.4	1.1	-	0.4
89122	25.8	-	-	25.0	-	-	-	-	-	-
89123	-	-	-	-	-	-	-	-	-	0.2
89124	-	-	-	-	-	-	-	-	-	1.7
89130	-	-	-	-	-	-	-	-	-	-
89131	-	-	-	-	-	-	-	-	-	-
89132	-	-	-	-	-	-	-	-	0.1	0.8
89133	-	0.9	-	0.2	3.7	-	-	11.6	7.4	4.4
89135	-	-	0.8	6.2	58.4	8.9	4.0	-	1.4	-
89136	-	-	-	-	2.9	-	19.2	-	6.1	-
89138	-	-	-	-	-	-	-	-	-	-
(ii) TYWI										
88111	60.1	-	25.4	-	-	-	-	-	-	-
88116	-	-	-	-	-	-	-	-	-	-
89141	-	-	-	13.5	-	-	-	-	-	1.1
89142	5.6	5.5	4.1	-	-	-	-	-	-	-
89143	3.5	58.8	-	-	-	-	-	-	-	-
89144	-	-	-	-	-	-	-	-	-	1.7
89145	-	-	-	-	-	-	-	-	-	-
89147	-	7.3	1.2	-	0.1	1.0	-	64.4	11.2	0.2
89148	-	-	-	-	-	-	-	-	-	10.7
89149	0.3	5.2	2.5	12.9	1.7	0.2	-	29.3	0.4	3.5
88085	-	-	-	-	-	-	-	-	-	-

4. Sites without data

For modelling purposes, the unmonitored river reaches within the Teifi and the Tywi have been divided into Hydrological Response Units (HRUs). These are hydrologically independent as defined by topography, with no cross-boundary inputs, and drainage only to an identified location on a stream network. They were derived using an automated procedure using the 50m spatial resolution Digital Terrain Model. The procedure involves moving up a river reach and accumulating the drainage area until an area threshold, in this case set at 2.5 sq km, is reached. At this stage, a new unit is defined. Each HRU is identifiable with a piece of landscape, such as a small catchment or hillslope on either side of the river. The procedure tends to generate most units close to the area threshold, but with a tail of smaller areas.

The generated HRUs for the Teifi and Tywi are shown, respectively, in Figs. 18 and 19. Streamflow chemistry for these HRUs are estimated according to relationships between streamflow chemistry and catchment characteristics derived from the Welsh Acid Waters Survey catchments.

Empirical relationships between water quality and catchment characteristics

While sufficient data are available to run the MAGIC model for a number of sites in Wales, notably the Welsh Acid Waters Survey (WAWS) catchments, these data are not fully available for modelling at the scale of a large catchment such as the Tywi, nor would it be appropriate to run MAGIC at this scale.

To provide estimates of water quality at large catchment scale, empirical relationships are sought between catchment characteristics and streamwater quality. The parameters of these relationships are estimated for the WAWS catchments, using both present day streamwater quality data and values obtained using MAGIC under scenarios of interest. These relationships are assumed to be generally applicable, and are used to simulate contaminant concentrations elsewhere, in particular for each HRU.

The concentration of contaminants in streamwater is determined largely by atmospheric inputs, soil and geological characteristics and land use and management, so these variables, if available, are potentially useful in the empirical relationships sought.

Catchment characteristics

The MAGIC model requires as input:

a. Annual atmospheric wet and dry deposition
b. Annual effective rainfall
c. CEC, bulk density and carbon dioxide partial pressure
d. Land use characteristics, particularly sequences of planting and felling of forestry

These data are available at the WAWS catchments, but at most unmonitored sites there is no information on contaminant concentrations in drainage water, nor of the soil properties referred to. There is, however, spatial information on atmospheric deposition and effective rainfall.

There are also at both monitored and unmonitored sites, further soils, geological and land cover data. These include:

a. The HOST soils classification
b. The ITE land cover classification

Data potentially available include the MAFF small areas database giving cropping and stocking rates by grouped parish. This would augment the land cover data, but has not been secured for the present study.

<u>Empirical relationships</u>

Certain characteristics of catchments have been shown to be broadly associated with particular streamwater chemical signatures, and the mechanism by which this occurs is often quite well known. The extensive WAWS database enables a wide range of relationships to be explored, with the potential for providing simple empirical quantitative regressions between catchment characteristics and water quality, and also of indicating unexpected relationships.

As a preliminary to fitting an empirical model, it is useful to plot water quality variables against each other and against catchment characteristics. Visual inspection of the data will reveal any obvious structure and also the presence of any anomalous data points. The dependent variables of interest are concentrations of those contaminants which are associated with streamwater acidification, and the possible explanatory variables, the soils, land use and other catchment characteristics described. Appendices 1 to 7 show a wide range of plots of this sort, based on annual median concentrations for the 102 WAWS catchments.

In general these plots are characterised by the presence of small numbers of outlying values for either dependent or explanatory variables. The former are partly explained by major geological and climatic differences between a few southern and eastern catchments and the remainder. The percentage of many land cover or soil classes is frequently very small or zero. Any apparent relationships between water quality and catchment variables are generally weak, though there are numerous instances where a high proportion of some explanatory variable is never associated with a high value of the dependent variable. At low proportions, the response depends on the nature of the remaining land use or soils proportions. In this case the situation is complicated by the correlation between the values of the explanatory variables, which in the case of proportions must sum to 1. As an example, high proportions of moorland grass or shrub moor are always associated with low nitrate concentrations. This is expected for nitrate, but is also true of sulphate, which is less expected. A clear positive association between variables is rarely seen, an example being the relationship between dissolved organic carbon concentration and the proportion of HOST class 29, which is raw peat. This relationship is unsurprising.

A first choice of quantitative relationship between explanatory and dependent variables, taking no account of possible process understanding, is a linear regression equation. This is capable of simulating simple straight line relationships between variables. Although there are a large number of potential explanatory variables, those which have significant predictive power can be estimated by an automated stepwise regression procedure. This successively adds and removes variables to a regression equation, accepting only those which give a statistically significant regression coefficient. The procedure is capable of producing no relationship at all if none of the potential explanatory variables appears to have any predictive power.

This approach has been used for each individual water quality variable measured at the WAWS catchments. The potential explanatory variables used are those which are available for unmonitored catchments, namely annual rainfall, atmospheric deposition, HOST class and land cover class. Other possible variables not used include a number associated with catchment topography and size.

<u>Regression relationships</u>

The results of stepwise regression fitting are shown in Table 6 and Figure 20. Results for ammonia and nitrite are excluded from Table 6 since the results are distorted by an outlier.

In the results presented, data from all catchments having streamwater hardness greater than 40 mg/l CaCO3 have been omitted. Preliminary analysis suggested that these catchments were atypical and distorted the regression relationships when combined with the remainder. However, it is likely that in the final analysis of these data, information from these catchments will be included in predictors of water quality within the Tywi catchment. In a further restriction on the analysis, a number of deposition variables have been omitted. The correlation between wet deposition loads of Ca, Mg, Na, Cl and K is over 0.95, so only Ca is included in the list of potential explanatory variables. This means that any direct causal relationship between, say input Cl load and streamwater Cl concentrations would not be apparent from any fitted regression relationship. Similarly, NH4 wet deposition is omitted because of its high correlation with NO3 wet deposition, and HOST classes 19 and 22 are omitted because of their high correlation with HOST class 17.

The formal analysis generally provides a fit to the contaminant concentrations with an R^2 value in excess of 0.7. The only regression which is not significant as judged by an F-test of the residuals is that for zinc. The raw regression relationships produced using this analysis may be used directly to estimate contaminant concentrations for each HRU, since values of the necessary explanatory variables are available. However, the robustness and suitability of these relationships needs to be assessed.

pH

This is expected to be related largely to soil characteristics. Land cover may be related to pH, but the ecology at a location is partly a response to soil acidity rather than conversely. The significant HOST classes are those with a high peat content (15, 27 and 29), high proportions of which tend to reduce the pH. HOST class 24, an important poorly drained mineral soil shows a positive association with pH. Land cover classes associated with an

Table 6 Restricted stepwise regression of WAWS water quality variables on catchment characteristics

Table 6(a) pH

```
Call: "Regression with dependent variable pH"
Residuals:
    Min      1Q Median     3Q   Max
 -1.108 -0.2091  0.072 0.2331 0.651
```

Coefficients:

	Value	Std. Error	t value	Pr(>|t|)
Intercept	6.1538	0.4224	14.5692	0.0000
% HOST class 4	-0.0179	0.0082	-2.1916	0.0314
% HOST class 15	-0.0095	0.0026	-3.6074	0.0005
% HOST class 24	0.0287	0.0165	1.7436	0.0852
% HOST class 27	-0.0197	0.0101	-1.9528	0.0544
% HOST class 29	-0.0108	0.0030	-3.5805	0.0006
% Grass Heath	0.0417	0.0146	2.8668	0.0053
% Moorland Grass	0.0102	0.0036	2.8851	0.0051
% Open Shrub Moor	0.0126	0.0036	3.4459	0.0009
% Dense Shrub Moor	0.0163	0.0071	2.2992	0.0242
% Bracken	0.0270	0.0139	1.9351	0.0566
% Deciduous Woodland	0.0182	0.0076	2.3760	0.0200
H wet dep	3.1596	0.7719	4.0931	0.0001
SO2 S dry dep	-0.1787	0.0652	-2.7421	0.0076
NO2 N dry dep	0.7594	0.3398	2.2350	0.0283
Annual rainfall mm	-0.0004	0.0001	-2.7359	0.0077

Residual standard error: 0.3726 on 78 degrees of freedom
Multiple R-Squared: 0.5054
F-statistic: 5.314 on 15 and 78 degrees of freedom, the p-value is 3.532e-07

Table 6(b) Conductivity

```
Call: "Regression with dependent variable conductivity"
Residuals:
    Min     1Q  Median    3Q  Max
 -13.44 -3.939 -0.1613 3.312 17.1
```

Coefficients:

	Value	Std. Error	t value	Pr(>|t|)
Intercept	59.0774	10.0535	5.8763	0.0000
% HOST class 15	-0.2953	0.0539	-5.4754	0.0000
% HOST class 17	-0.2021	0.0647	-3.1216	0.0025
% HOST class 29	-0.2045	0.0532	-3.8439	0.0002
% Grass Heath	0.4206	0.2692	1.5625	0.1222
% Mown/Grazed Turf	0.5525	0.1414	3.9087	0.0002
% Meadow/Seminatural	-0.4841	0.1864	-2.5974	0.0112
% Moorland Grass	-0.1800	0.0618	-2.9120	0.0047
% Open Shrub Moor	-0.1720	0.0655	-2.6279	0.0103
% Bracken	-0.5082	0.2689	-1.8901	0.0625
% Deciduous Woodland	0.3884	0.1346	2.8855	0.0051
SO4 S wet dep	1.0146	0.3199	3.1721	0.0022
PO4 P wet dep	288.1649	74.5897	3.8633	0.0002
SO2 S dry dep	-4.8943	1.1328	-4.3205	0.0000
NO2 N dry dep	29.3681	5.4096	5.4289	0.0000
Annual rainfall mm	-0.0164	0.0022	-7.3510	0.0000

Residual standard error: 6.589 on 78 degrees of freedom
Multiple R-Squared: 0.8137
F-statistic: 22.7 on 15 and 78 degrees of freedom, the p-value is 0

Table 6(c) Hardness

Call: "Regression with dependent variable hardness"
Residuals:

Min	1Q	Median	3Q	Max
-7.916	-1.681	-0.07087	1.609	12.09

Coefficients:

	Value	Std. Error	t value	Pr(>|t|)
Intercept	1.0484	4.5770	0.2291	0.8194
% HOST class 15	-0.1383	0.0235	-5.8924	0.0000
% HOST class 17	-0.0780	0.0285	-2.7324	0.0077
% HOST class 29	-0.1034	0.0267	-3.8772	0.0002
% Grass Heath	0.4335	0.1239	3.5001	0.0008
% Mown/Grazed Turf	0.2516	0.0659	3.8154	0.0003
% Meadow/Seminatural	-0.1380	0.0810	-1.7038	0.0923
% Dense Shrub Moor	0.1611	0.0572	2.8142	0.0062
% Deciduous Woodland	0.2761	0.0514	5.3723	0.0000
H wet dep	17.2916	6.3521	2.7222	0.0080
PO4 P wet dep	178.3669	34.4134	5.1831	0.0000
SO2 S dry dep	-1.3034	0.5281	-2.4680	0.0157
NO2 N dry dep	11.4424	2.5018	4.5737	0.0000
Annual rainfall mm	-0.0061	0.0011	-5.8473	0.0000

Residual standard error: 3.13 on 80 degrees of freedom
Multiple R-Squared: 0.7391
F-statistic: 17.43 on 13 and 80 degrees of freedom, the p-value is 0

Table 6(d) Calcium

Call: "Regression with dependent variable Ca"
Residuals:

Min	1Q	Median	3Q	Max
-2.175	-0.5102	-0.04258	0.3331	2.774

Coefficients:

	Value	Std. Error	t value	Pr(>|t|)
Intercept	-1.2997	1.6680	-0.7792	0.4382
% HOST class 15	-0.0439	0.0068	-6.4228	0.0000
% HOST class 17	-0.0243	0.0080	-3.0286	0.0033
% HOST class 29	-0.0337	0.0080	-4.2318	0.0001
% Grass Heath	0.1215	0.0344	3.5321	0.0007
% Mown/Grazed Turf	0.0688	0.0190	3.6234	0.0005
% Meadow/Seminatural	-0.0421	0.0231	-1.8212	0.0724
% Dense Shrub Moor	0.0483	0.0159	3.0376	0.0032
% Deciduous Woodland	0.0742	0.0145	5.1050	0.0000
Ca wet dep	-0.4120	0.2454	-1.6787	0.0972
SO4 S wet dep	0.1959	0.0827	2.3708	0.0202
PO4 P wet dep	74.9124	9.6708	7.7463	0.0000
SO2 S dry dep	-0.4006	0.1747	-2.2932	0.0245
NO2 N dry dep	2.1661	0.7332	2.9544	0.0041
Annual rainfall mm	-0.0015	0.0003	-4.8105	0.0000

Residual standard error: 0.8752 on 79 degrees of freedom
Multiple R-Squared: 0.7476
F-statistic: 16.71 on 14 and 79 degrees of freedom, the p-value is 0

Table 6(e) Alkalinity

Call: "Regression with dependent variable alkalinity"
Residuals:

Min	1Q	Median	3Q	Max
-5.027	-1.034	-0.09091	1.059	9.34

Coefficients:

	Value	Std. Error	t value	Pr(>|t|)
Intercept	-0.3861	5.6549	-0.0683	0.9458
% HOST class 4	-0.1605	0.0663	-2.4228	0.0179
% HOST class 7	-5.4011	3.5750	-1.5108	0.1352
% HOST class 10	-0.6223	0.2967	-2.0974	0.0394
% HOST class 15	-0.1888	0.0339	-5.5725	0.0000
% HOST class 17	-0.1538	0.0367	-4.1908	0.0001
% HOST class 27	-0.1357	0.0749	-1.8120	0.0741
% HOST class 29	-0.1581	0.0361	-4.3774	0.0000
% Grass Heath	0.3191	0.1113	2.8674	0.0054
% Mown/Grazed Turf	0.2034	0.0569	3.5766	0.0006
% Meadow/Seminatural	-0.1371	0.0739	-1.8548	0.0677
% Dense Shrub Moor	0.1352	0.0521	2.5957	0.0114
% Deciduous Woodland	0.1086	0.0472	2.3011	0.0242
% Coniferous Woodland	-0.0479	0.0228	-2.1000	0.0392
H wet dep	27.5334	8.9247	3.0851	0.0029
Ca wet dep	-1.1345	0.6637	-1.7092	0.0917
PO4 P wet dep	182.2503	30.1413	6.0465	0.0000
NH3 N dry dep	0.4738	0.2180	2.1728	0.0330
SO2 S dry dep	-1.6107	0.5149	-3.1280	0.0025
NO2 N dry dep	6.0224	2.4408	2.4674	0.0160
Annual rainfall mm	-0.0023	0.0011	-1.9919	0.0501

Residual standard error: 2.586 on 73 degrees of freedom
Multiple R-Squared: 0.7326
F-statistic: 9.998 on 20 and 73 degrees of freedom, the p-value is 8.16e-14

Table 6(f) Total Oxidised Nitrogen

Call: "Regression with dependent variable TON"
Residuals:

Min	1Q	Median	3Q	Max
-0.3282	-0.08338	0.007041	0.06764	0.3505

Coefficients:

	Value	Std. Error	t value	Pr(>|t|)
Intercept	-0.0355	0.1717	-0.2066	0.8368
% HOST class 15	-0.0036	0.0009	-3.9720	0.0002
% HOST class 29	-0.0022	0.0010	-2.1781	0.0323
% Unclassified	-0.0086	0.0033	-2.6008	0.0111
% Grass Heath	0.0110	0.0050	2.1841	0.0318
% Moorland Grass	-0.0051	0.0009	-5.5037	0.0000
% Open Shrub Moor	-0.0048	0.0013	-3.6846	0.0004
% Bracken	-0.0130	0.0051	-2.5524	0.0126
H wet dep	1.1578	0.5375	2.1541	0.0342
Ca wet dep	0.1004	0.0387	2.5976	0.0111
SO4 S wet dep	-0.0459	0.0174	-2.6471	0.0098
NH3 N dry dep	0.0253	0.0099	2.5488	0.0127
NO2 N dry dep	0.3558	0.1201	2.9635	0.0040

Residual standard error: 0.1364 on 81 degrees of freedom
Multiple R-Squared: 0.7147
F-statistic: 16.91 on 12 and 81 degrees of freedom, the p-value

Table 6(g) Nitrate

Call: "Regression with dependent variable NO3"

Residuals:

Min	1Q	Median	3Q	Max
-0.3312	-0.08347	0.006889	0.06824	0.3507

Coefficients:

	Value	Std. Error	t value	Pr(>|t|)
Intercept	-0.0223	0.1721	-0.1295	0.8973
% HOST class 15	-0.0036	0.0009	-3.9989	0.0001
% HOST class 29	-0.0022	0.0010	-2.1934	0.0311
% Unclassified	-0.0086	0.0033	-2.5919	0.0113
% Grass Heath	0.0110	0.0051	2.1645	0.0334
% Moorland Grass	-0.0051	0.0009	-5.4926	0.0000
% Open Shrub Moor	-0.0048	0.0013	-3.6931	0.0004
% Bracken	-0.0133	0.0051	-2.5911	0.0113
H wet dep	1.1651	0.5389	2.1621	0.0336
Ca wet dep	0.0998	0.0388	2.5760	0.0118
SO4 S wet dep	-0.0462	0.0174	-2.6556	0.0095
NH3 N dry dep	0.0252	0.0099	2.5305	0.0133
NO2 N dry dep	0.3488	0.1204	2.8978	0.0048

Residual standard error: 0.1368 on 81 degrees of freedom
Multiple R-Squared: 0.7138
F-statistic: 16.83 on 12 and 81 degrees of freedom, the p-value is 0

Table 6(h) Chloride

Call: "Regression with dependent variable Cl"

Residuals:

Min	1Q	Median	3Q	Max
-3.318	-0.5128	-0.08422	0.4714	3.305

Coefficients:

	Value	Std. Error	t value	Pr(>|t|)
Intercept	18.9395	2.0163	9.3931	0.0000
% HOST class 4	0.0535	0.0257	2.0835	0.0406
% HOST class 15	-0.0209	0.0082	-2.5354	0.0133
% HOST class 17	-0.0249	0.0103	-2.4232	0.0178
% Unclassified	-0.0529	0.0298	-1.7723	0.0804
% Grass Heath	-0.0765	0.0439	-1.7410	0.0857
% Moorland Grass	-0.0755	0.0113	-6.7048	0.0000
% Open Shrub Moor	-0.0608	0.0115	-5.2850	0.0000
% Dense Shrub Moor	-0.0542	0.0207	-2.6181	0.0107
% Bracken	-0.1541	0.0438	-3.5158	0.0007
% Deciduous Woodland	-0.0528	0.0245	-2.1552	0.0343
H wet dep	8.6670	4.7909	1.8091	0.0744
SO4 S wet dep	0.2784	0.1499	1.8575	0.0671
NO3 N wet dep	-0.9886	0.3821	-2.5871	0.0116
NH3 N dry dep	0.2042	0.0835	2.4443	0.0168
SO2 S dry dep	-0.9437	0.2043	-4.6191	0.0000
NO2 N dry dep	1.8038	1.0363	1.7407	0.0858
Annual rainfall mm	-0.0022	0.0005	-4.6107	0.0000

Residual standard error: 1.116 on 76 degrees of freedom
Multiple R-Squared: 0.8209
F-statistic: 20.49 on 17 and 76 degrees of freedom, the p-value is 0

Table 6(i) Sodium

Call: "Regression with dependent variable Na"

Residuals:

Min	1Q	Median	3Q	Max
-1.558	-0.3105	-0.02988	0.2998	1.891

Coefficients:

	Value	Std. Error	t value	Pr(>|t|)
Intercept	9.4973	0.8973	10.5838	0.0000
% HOST class 15	-0.0130	0.0040	-3.2456	0.0017
% HOST class 17	-0.0082	0.0051	-1.6127	0.1108
% Unclassified	-0.0233	0.0146	-1.5954	0.1147
% Meadow/Seminatural	-0.0374	0.0153	-2.4428	0.0168
% Moorland Grass	-0.0298	0.0045	-6.6119	0.0000
% Open Shrub Moor	-0.0236	0.0054	-4.3592	0.0000
% Dense Shrub Moor	-0.0315	0.0096	-3.2922	0.0015
% Bracken	-0.0478	0.0221	-2.1644	0.0335
H wet dep	4.4622	2.3395	1.9073	0.0602
SO4 S wet dep	0.1475	0.0697	2.1172	0.0374
NO3 N wet dep	-0.4855	0.1831	-2.6510	0.0097
NH3 N dry dep	0.1385	0.0408	3.3939	0.0011
SO2 S dry dep	-0.5048	0.1022	-4.9404	0.0000
NO2 N dry dep	1.4349	0.4917	2.9184	0.0046
Annual rainfall mm	-0.0013	0.0002	-5.5430	0.0000

Residual standard error: 0.5598 on 78 degrees of freedom
Multiple R-Squared: 0.8342
F-statistic: 26.16 on 15 and 78 degrees of freedom, the p-value is 0

Table 6(j) Sulphate

Call: "Regression with dependent variable SO4"

Residuals:

Min	1Q	Median	3Q	Max
-1.952	-0.8292	0.01025	0.648	2.955

Coefficients:

	Value	Std. Error	t value	Pr(>|t|)
Intercept	22.4727	2.6400	8.5125	0.0000
% HOST class 5	0.3042	0.1407	2.1627	0.0338
% HOST class 10	-0.3047	0.1311	-2.3235	0.0229
% HOST class 15	-0.0615	0.0157	-3.9103	0.0002
% HOST class 17	-0.0443	0.0179	-2.4816	0.0153
% HOST class 24	-0.2634	0.0542	-4.8648	0.0000
% HOST class 26	-0.0320	0.0167	-1.9204	0.0587
% HOST class 29	-0.0584	0.0165	-3.5328	0.0007
% Moorland Grass	-0.0610	0.0122	-5.0133	0.0000
% Open Shrub Moor	-0.0471	0.0133	-3.5393	0.0007
% Dense Shrub Moor	-0.0371	0.0223	-1.6620	0.1007
% Bracken	-0.1637	0.0563	-2.9080	0.0048
% Deciduous Woodland	0.0559	0.0244	2.2909	0.0248
% Coniferous Woodland	-0.0182	0.0121	-1.5005	0.1377
% Upland Bog	-0.0668	0.0257	-2.5940	0.0114
Ca wet dep	-2.1773	0.2243	-9.7057	0.0000
SO4 S wet dep	1.3498	0.1757	7.6829	0.0000
NO3 N wet dep	-2.0851	0.4389	-4.7505	0.0000
PO4 P wet dep	-39.4423	14.0794	-2.8014	0.0065
Annual rainfall mm	-0.0018	0.0005	-3.9852	0.0002

Residual standard error: 1.144 on 74 degrees of freedom
Multiple R-Squared: 0.8476
F-statistic: 21.67 on 19 and 74 degrees of freedom, the p-value is 0

Table 6(k) Potassium

Call: "Regression with dependent variable K"

Residuals:

Min	1Q	Median	3Q	Max
-0.2655	-0.06413	-0.009864	0.07234	0.4788

Coefficients:

	Value	Std. Error	t value	Pr(>|t|)
Intercept	1.6817	0.2303	7.3012	0.0000
% HOST class 10	0.0234	0.0086	2.7054	0.0084
% HOST class 24	0.0088	0.0051	1.7153	0.0903
% Unclassified	-0.0211	0.0043	-4.9104	0.0000
% Grass Heath	-0.0336	0.0057	-5.8672	0.0000
% Meadow/Seminatural	-0.0259	0.0049	-5.2775	0.0000
% Rough/Marsh Grass	-0.0127	0.0054	-2.3474	0.0215
% Moorland Grass	-0.0161	0.0020	-8.1876	0.0000
% Open Shrub Moor	-0.0167	0.0021	-7.9551	0.0000
% Dense Shrub Moor	-0.0154	0.0025	-6.0820	0.0000
% Deciduous Woodland	-0.0180	0.0028	-6.3890	0.0000
% Coniferous Woodland	-0.0161	0.0020	-7.8594	0.0000
% Upland Bog	-0.0180	0.0031	-5.8975	0.0000
SO4 S wet dep	0.0267	0.0048	5.6124	0.0000
SO2 S dry dep	-0.0920	0.0186	-4.9439	0.0000
NO2 N dry dep	0.6450	0.0895	7.2036	0.0000
Annual rainfall mm	-0.0002	0.0000	-4.1933	0.0001

Residual standard error: 0.1136 on 77 degrees of freedom
Multiple R-Squared: 0.7649
F-statistic: 15.66 on 16 and 77 degrees of freedom, the p-value is 0

Table 6(l) Magnesium

Call: "Regression with dependent variable Mg"

Residuals:

Min	1Q	Median	3Q	Max
-0.6461	-0.1466	-0.04144	0.1334	1.16

Coefficients:

	Value	Std. Error	t value	Pr(>|t|)
Intercept	3.1530	0.4551	6.9284	0.0000
% HOST class 15	-0.0038	0.0019	-1.9969	0.0493
% HOST class 29	-0.0046	0.0022	-2.1121	0.0378
% Unclassified	-0.0212	0.0090	-2.3624	0.0206
% Mown/Grazed Turf	0.0158	0.0064	2.4607	0.0160
% Meadow/Seminatural	-0.0294	0.0100	-2.9295	0.0044
% Rough/Marsh Grass	-0.0308	0.0138	-2.2307	0.0285
% Moorland Grass	-0.0145	0.0035	-4.1177	0.0001
% Open Shrub Moor	-0.0146	0.0043	-3.3860	0.0011
% Coniferous Woodland	-0.0116	0.0042	-2.7487	0.0074
% Upland Bog	-0.0130	0.0070	-1.8610	0.0665
H wet dep	1.9557	0.5845	3.3461	0.0013
SO2 S dry dep	-0.1803	0.0495	-3.6385	0.0005
NO2 N dry dep	1.1526	0.2437	4.7306	0.0000
Annual rainfall mm	-0.0006	0.0001	-5.8359	0.0000

Residual standard error: 0.2979 on 79 degrees of freedom
Multiple R-Squared: 0.7084
F-statistic: 13.71 on 14 and 79 degrees of freedom, the p-value is 8.882e-16

Table 6(m) Aluminium

Call: "Regression with dependent variable Al"
Residuals:

Min	1Q	Median	3Q	Max
-0.07856	-0.02273	0.0001979	0.01841	0.1751

Coefficients:

	Value	Std. Error	t value	Pr(>|t|)
Intercept	-0.0234	0.0352	-0.6640	0.5085
% HOST class 17	-0.0010	0.0003	-3.6556	0.0004
% HOST class 24	-0.0032	0.0017	-1.9361	0.0562
% HOST class 27	0.0026	0.0009	2.8393	0.0057
% Mown/Grazed Turf	0.0018	0.0008	2.4449	0.0166
% Coniferous Woodland	0.0023	0.0003	8.4856	0.0000
H wet dep	-0.4206	0.1652	-2.5452	0.0128
SO4 S wet dep	-0.0075	0.0044	-1.6985	0.0931
NO3 N wet dep	0.0389	0.0115	3.3726	0.0011
SO2 S dry dep	0.0171	0.0049	3.4999	0.0007

Residual standard error: 0.03958 on 84 degrees of freedom
Multiple R-Squared: 0.5219
F-statistic: 10.19 on 9 and 84 degrees of freedom, the p-value is 1.906e-10

Table 6(n) Dissolved Organic Carbon

Call: "Regression with dependent variable DOC"
Residuals:

Min	1Q	Median	3Q	Max
-1.344	-0.4105	-0.002304	0.3535	1.597

Coefficients:

	Value	Std. Error	t value	Pr(>|t|)
Intercept	-1.3580	1.1565	-1.1742	0.2438
% HOST class 4	0.0300	0.0179	1.6756	0.0978
% HOST class 10	0.1271	0.0707	1.7969	0.0762
% HOST class 15	0.0261	0.0105	2.4895	0.0149
% HOST class 17	0.0297	0.0116	2.5478	0.0128
% HOST class 24	0.0847	0.0302	2.8051	0.0063
% HOST class 26	0.0466	0.0096	4.8744	0.0000
% HOST class 29	0.0606	0.0108	5.6159	0.0000
% Unclassified	0.0269	0.0155	1.7285	0.0878
% Moorland Grass	0.0135	0.0049	2.7612	0.0072
% Bracken	0.0485	0.0232	2.0912	0.0397
% Upland Bog	0.0671	0.0132	5.0768	0.0000
H wet dep	-8.6116	2.5810	-3.3365	0.0013
SO4 S wet dep	-0.1523	0.0845	-1.8022	0.0753
NO3 N wet dep	0.7827	0.2241	3.4935	0.0008

Residual standard error: 0.6363 on 79 degrees of freedom
Multiple R-Squared: 0.7709
F-statistic: 18.98 on 14 and 79 degrees of freedom, the p-value is 0

Table 6(o) Zinc

Call: "Regression with dependent variable Zn"

Residuals:

Min	1Q	Median	3Q	Max
-20.42	-8.124	-2.101	1.662	139.3

Coefficients:

	Value	Std. Error	t value	Pr(>|t|)
Intercept	76.9352	20.3264	3.7850	0.0003
% HOST class 15	-0.2866	0.1371	-2.0902	0.0395
% HOST class 17	-0.3120	0.1547	-2.0173	0.0467
% HOST class 29	-0.2325	0.1436	-1.6187	0.1091
NO3 N wet dep	-5.4494	2.4830	-2.1947	0.0308
NH3 N dry dep	-2.3092	1.0475	-2.2045	0.0301

Residual standard error: 19.11 on 88 degrees of freedom
Multiple R-Squared: 0.1237
F-statistic: 2.484 on 5 and 88 degrees of freedom, the p-value is 0.03745

Table 6(p) Manganese

Call: "Regression with dependent variable Mn"

Residuals:

Min	1Q	Median	3Q	Max
-66.37	-18.02	-2.349	12.54	87.27

Coefficients:

	Value	Std. Error	t value	Pr(>|t|)
Intercept	177.9911	38.5303	4.6195	0.0000
% HOST class 15	-0.9071	0.2253	-4.0257	0.0001
% HOST class 17	-1.1471	0.2993	-3.8332	0.0003
% HOST class 24	-3.0512	1.3480	-2.2634	0.0264
% HOST class 26	-0.9152	0.3363	-2.7211	0.0080
% HOST class 27	-2.4989	0.7403	-3.3756	0.0011
% Mown/Grazed Turf	-1.3059	0.6435	-2.0292	0.0458
% Rough/Marsh Grass	3.1598	1.1931	2.6485	0.0098
% Moorland Grass	-0.5770	0.2788	-2.0698	0.0417
% Open Shrub Moor	-0.6150	0.3032	-2.0287	0.0459
% Dense Shrub Moor	-1.6189	0.5479	-2.9547	0.0041
% Deciduous Woodland	-1.1711	0.6488	-1.8052	0.0749
% Upland Bog	2.8603	0.6654	4.2986	0.0000
H wet dep	207.8535	121.2290	1.7146	0.0903
SO4 S wet dep	-6.2341	2.9656	-2.1022	0.0387

Residual standard error: 30.82 on 79 degrees of freedom
Multiple R-Squared: 0.5043
F-statistic: 5.742 on 14 and 79 degrees of freedom, the p-value is 1.526e-07

Table 6(q) Iron

Call: "Regression with dependent variable Fe"
Residuals:

Min	1Q	Median	3Q	Max
-303	-52.26	1.692	61.76	270.1

Coefficients:

	Value	Std. Error	t value	Pr(>|t|)
Intercept	644.7074	106.5229	6.0523	0.0000
% HOST class 4	-4.4561	1.9875	-2.2420	0.0278
% HOST class 7	-393.2391	134.4786	-2.9242	0.0045
% HOST class 10	-16.7331	9.5836	-1.7460	0.0848
% HOST class 15	-6.2210	0.7628	-8.1559	0.0000
% HOST class 17	-5.9211	0.8591	-6.8919	0.0000
% HOST class 24	-9.9017	4.4986	-2.2011	0.0307
% HOST class 26	-4.0410	1.2416	-3.2546	0.0017
% HOST class 27	-12.3382	2.6668	-4.6267	0.0000
% Grass Heath	7.6248	4.0464	1.8844	0.0633
% Rough/Marsh Grass	7.0570	3.9865	1.7702	0.0806
% Deciduous Woodland	-2.7223	1.6799	-1.6205	0.1092
% Coniferous Woodland	-1.5210	0.7785	-1.9537	0.0544
% Upland Bog	22.4121	2.2408	10.0019	0.0000
H wet dep	-416.1719	196.7655	-2.1151	0.0377
SO2 S dry dep	-31.6796	16.1446	-1.9622	0.0533
NO2 N dry dep	171.5320	87.0954	1.9695	0.0525

Residual standard error: 101 on 77 degrees of freedom
Multiple R-Squared: 0.7942
F-statistic: 18.57 on 16 and 77 degrees of freedom, the p-value is 0

increase in pH are deciduous woodland, bracken and some moorland classes. This is not intuitively obvious, and needs to be interpreted in the light of other variables. Low pH is also strongly associated with high wet deposition of H^+, and loosely associated with other forms of atmospheric deposition. Finally, low pH has some association with high rainfall.

Conductivity, hardness, calcium and alkalinity

These variables are closely related to each other (correlation > .9). They are also related to pH, but non-linearly, a log-log plot of hydrogen ion concentration against any of them giving an approximate straight line.

In terms of their relationship to catchment characteristics, these variables show a similar pattern to pH. The influence of HOST class is similar in the estimated regression relationship, but the land cover coefficients show a negative relationship with some low productivity grasslands and a positive association with good grassland (mown/grazed turf) and deciduous woodland. There is a strong negative association with annual rainfall, and some association with deposition variables. As with pH the atmospheric deposition coefficients are difficult to interpret.

TON/Nitrate

High concentrations of this are generally due to diffuse agricultural sources in relatively productive farmland, although there is evidence of nitrate saturation in some upland areas. Raised nitrate concentrations are also associated with timber harvesting. The explanatory variables show a negative association with peaty soils (HOST classes 15 and 29) and with some low productivity moorland land cover variables, and mixed association with atmospheric deposition.

Chloride/Sodium

Chloride has no natural source within most catchments, its main source being atmospheric. In the WAWS catchments, concentrations are highly correlated with sodium. Sodium and calcium are well correlated for most catchments, but a number have a much higher Ca/Na ratio, indicating a within-catchment Ca source.

Chloride concentration has a negative association with some moorland land cover variables, with rainfall and with one peaty soil (HOST class 15). Calcium wet deposition load (as a surrogate for chloride) does not appear amongst the explanatory variables selected, though other deposition variables are significant.

Sulphate

This is loosely associated with cation concentrations. It has a negative association with peaty soils, rainfall, some moorland land cover classes, and wet deposition of calcium. It has a strong positive association with wet deposition of sulphur.

Potassium/magnesium

These minor cations are associated with low rainfall, mineral soils and productive land.

Aluminium

This is inversely related to pH, with a log-log plot showing a straight line. The poor regression relationship shows a strong association with the proportion of coniferous woodland, but only one peaty soil variable (HOST class 27) is selected as significant. There is some negative association with mineral soils.

DOC
Dissolved organic carbon is known to be generally associated with the decomposition of organic matter, and in particular the breakdown of peat. The strongest associations given by the selected regression equation are with upland bog and raw peat, which is consistent with this causal understanding. Moorland grass and other peaty soils also show association.

Zinc, manganese and iron
Zinc is the only contaminant for which the selected regression relationship is only marginally significant (p-value 0.03745). Manganese tends to be associated with upland bogs, and iron is very closely associated with upland bogs.

Most of the regression relationships selected by the stepwise procedure can be roughly explained in terms of existing understanding of the influence of certain soil, land cover and rainfall characteristics. However, in many cases the atmospheric deposition variables have significant explanatory power whose interpretation is not immediately apparent. A study of the spatial distribution of these variables in relation to catchment locations might be revealing.

Simulation for unobserved catchments and HRUs

The equations shown in Table 6 can be used to simulate water quality in unmonitored catchments and HRUs. However, a number of issues need to be addressed:

1. The training data from the WAWS catchments are not fully representative of a lowland catchment such as the Tywi. The regression relationships derived are most safely used within new catchments having broadly the characteristics of the WAWS population. Extrapolatory use of these relationships will give very uncertain simulations of water quality, because of the presence of catchment characteristics and contaminant sources not encountered in the WAWS catchments. With this in mind, it is hoped to include catchments upstream of some Environment Agency monitoring sites to extend the training sample.

2. The regression relationships produced are purely empirical and are capable of giving simulations which do not satisfy sensible scientific constraints, such as charge balance. The extent of this problem is unknown at present, and there are means of overcoming it which will be to some extent subjective.

3. The possible importance of other catchment characteristics needs to be considered.

4. MAGIC scenarios for the WAWS catchments are obtained using assumptions about processes which may be broadly acceptable for upland catchments of the sort represented by the WAWS population. MAGIC may be less useful as a descriptor of processes occurring in low lying, more intensively managed land. Use of regression equations based on MAGIC scenario water quality simulations adds further uncertainty to HRU simulations.

6. MAGIC Application

The acidification model being used in this study is the Model of Acidification of Groundwater in Catchments (MAGIC). This is a dynamic model which has been developed to predict the response of soil and surface water to changing land use and acidic deposition.

The model consists of three basic steps:-

(i) Atmospheric deposition enters the soil compartment.

(ii) Equilibrium equations are used to calculate soil water chemistry.

(iii) The soil water is routed to the stream and the appropriate equilibrium equations are reapplied to calculate streamwater chemistry.

MAGIC uses a lumped approach in two ways:-

(i) A myriad of chemical and biological processes active in catchments are aggregated into a few readily - described processes.

(ii) The spatial heterogeneity of soil properties within the catchment is lumped to one set of soil parameters.

A set of equations quantitively describe the equilibruim soil processes and the chemical changes that occur as soil water enters the stream channel, a set of mass balance equations quantitively describe the catchment input-output relationships for base cations and strong acid anions in precipitation and streamwater, and a set of definitions relate the variables in the equilibruim equations to the variables in the mass-balance equations.

The application of MAGIC requires data describing surface water quality, rainfall chemistry and volume, soil physical and chemical characteristics and land use history. The model uses a lumped approach where the soil parameters used are considered to represent the whole catchment. In this particular application, a single soil layer structure has been used with an annual time step. A detailed description of the model and its application have been given elsewhere (Cosby et al., 1986; Hornberger et al., 1986; Cosby et al., 1990; Jenkins et al., 1990; Jenkins et al., 1997).

Calibration

The model has been calibrated against mean annual streamflow chemistry for the Welsh Acid Waters Monitoring sub-catchments within the Teifi and the Tywi (Table 3) using the data described in Section 2. Selectivity coefficients and weathering rates for the strong base cations (calcium, magnesium, sodium, and potassium) were optimized for each of the sub-catchments. The resulting values are shown in Table 7.

Graphs of predicted against observed streamflow determinand concentrations are shown in Figures 21, 22, and 23. As can be seen from Fig. 21, the model closely simulates the

Table 7 Optimized Selectivity Coefficients and Weathering Rates (meq/m**2/yr) for the Strong Base Cations

Site	Selectivity coefficients				Weathering rates				
	Ca	Mg	Na	K	Ca	Mg	Na	K	Total
34408	9.7	11.4	4.6	1.5	254	126	72	11	462
88085	12.3	13.0	5.3	1.2	360	311	56	2.0	730
88111	3.5	5.6	1.8	-1.7	4.5	41	78	0.1	123
88116	5.7	7.0	0.5	-0.9	65	93	63	0.4	221
89119	7.1	9.4	4.3	-0.1	90	112	65	6.7	273
89120	9.1	11.5	4.3	0.8	170	124	71	6.9	372
89121	5.8	8.6	3.9	-0.8	73	88	78	1.8	241
89121	5.8	8.2	3.0	-1.0	49	67	66	1.1	183
89123	4.5	7.0	2.2	-1.3	13	63	56	0.1	132
89124	5.1	7.8	2.4	-1.1	24	79	61	0.2	164
89130	5.9	8.9	3.7	-0.2	16	65	106	2.3	188
89131	5.7	9.5	5.4	0.57	43	81	76	2.7	203
89132	9.6	8.9	4.9	0.3	30	87	67	2.0	184
89133	6.3	9.5	4.4	0.29	145	118	15	8.5	286
89135	5.8	8.7	3.4	-0.5	29	104	66	10.3	210
89136	9.6	11.4	5.0	1.3	257	198	62	8.5	525
89138	6.3	8.1	3.4	-0.7	35	35	77	0.17	147
89141	9.3	12.1	4.6	1.7	182	190	86	14.0	471
89142	7.7	9.0	5.3	0.8	65	96	114	1.4	276
89143	4.8	7.3	2.7	-1.4	12	55	92	0.5	159
89144	6.5	8.5	3.1	-0.3	53	95	86	0.04	237
89145	8.7	10.2	4.8	1.0	72	90	93	0.8	256
89147	8.4	10.1	4.4	0.9	118	134	52	12.1	316
89148	8.7	10.0	3.1	1.0	197	140	96	8.6	441
89149	4.1	6.7	2.2	-1.7	0.9	82	84	1.5	169

observed base cation stream chemistry. Potassium was over predicted for some of the sites. However, given the scale of graph, the error was small, and comparable with that seen for the other cation simulations. Fig. 22 shows the simulation of the anion concentrations against the observed values along with percentage base saturation. These simulations also show good fits to observed data. However, this would be expected, given that the chloride and sulphate ions are treated conservatively, and that nitrate ion uptake was set to be the difference between the nitrate fluxes into the catchment and nitrate concentrations observed in the stream. One site gave higher predicted concentrations of sulphate than observed; this remains to be investigated.

Fig. 23 shows the observed against predicted streamflow ANC, pH and the sum of base cations. Also shown is the relationship between pH and ANC for the observed and simulated data. The majority of sites show a close fit between the observed and simulated ANC, with the exception of two low ANC values that are slightly overestimated. The observed against simulated plot of pH shows a bias in that pH is slightly over predicted. This is probably related to the observed relationship between pH and ANC that shows a higher ANC for a given value of pH, compared with the simulated data. A good fit between observed and predicted sum of base cations is obtained.

References

Cosby, J.B., Hornberger, G.M., Wright, R.F. and Galloway, J.N., 1986. Modelling the effects of acid deposition: control of long term sulphate dynamics by soil sulphate absorption, Water Res. Research, **22**, 1283-1291.

Cosby, J.B., Jenkins, A., Ferrier, R.C., Walker, T.A.B., and Miller, J.D., 1990. Modelling stream acidification in afforested catchments: long term reconstructions at two sites in central Scotland, J. Hydrology, **120**, 140-162.

Boorman, D.B., Hollis, J.M. and A. Lilly, 1995. Hydrology of soil types: a hydrologically-based classification of the soils of the United Kingdom. Institute of Hydrology Report no. 126, pp.137.

Devenish, M., 1986. The United Kingdom precipitation composition networks. LR 584 (AP). Warren Spring laboratory, Stevenage, UK.

Fuller, R.M., Groom, G.B. and Jones, A.R., 1994. The Land Cover Map of Great Britain: an automated classification of Landsat Thematic Mapper data. Photogrammetric Engineering and Remote Sensing, 60, 553-562.

Hornberger, G.M., Cosby, J.B., and Galloway, J.N., 1986. Modelling the effects of acid deposition: uncertainty and spatial variability of long term sulphur dynamics in a region, Wat. Res., **22**, 1293-1302.

IH, 1993. Hydrological data UK. Hydrometric Register and statistics 1986-1990. (Eds. T.J. Marsh and M.L. Lees). Natural Environment Research Council.

Jenkins, A., Cosby, J.B., Ferrier, R.C., Walker, T.A.B., Miller, J.D., 1990. Modelling stream acidification in afforested catchments: an assessment of the relative effects of acid deposition and afforestation, J. Hydrology, **120**, 163-181.

Jenkins, A., Renshaw, M., Helliwell, R., Sefton, C.E., Ferrier, R. and P. Swingewood, 1997. Modelling surface water acidification in the UK. Application of the MAGIC model to the Acid Waters Monitoring Network. Institute of Hydrology Report no. 131, pp.54.

Meteorological Office, 1991. Summary of rainfall data over the UK.

Simpson, E.A., 1978. The harmonisation of the monitoring of the quality of inland fresh waters. J. Instn. Engrs. Scient., 32, 57-66.

Thompson, N., Barrie, I.A. and M. Ayles, 1981. The Meteorological Office Rainfall and Evaporation Calculation System: MORECS. Hydrological Memorandum no. 45, pp. 72.

Figures

23. Predicted vs Observed Streamflow ANC, pH and the sum of the base cations, and the relationship between pH and ANC.

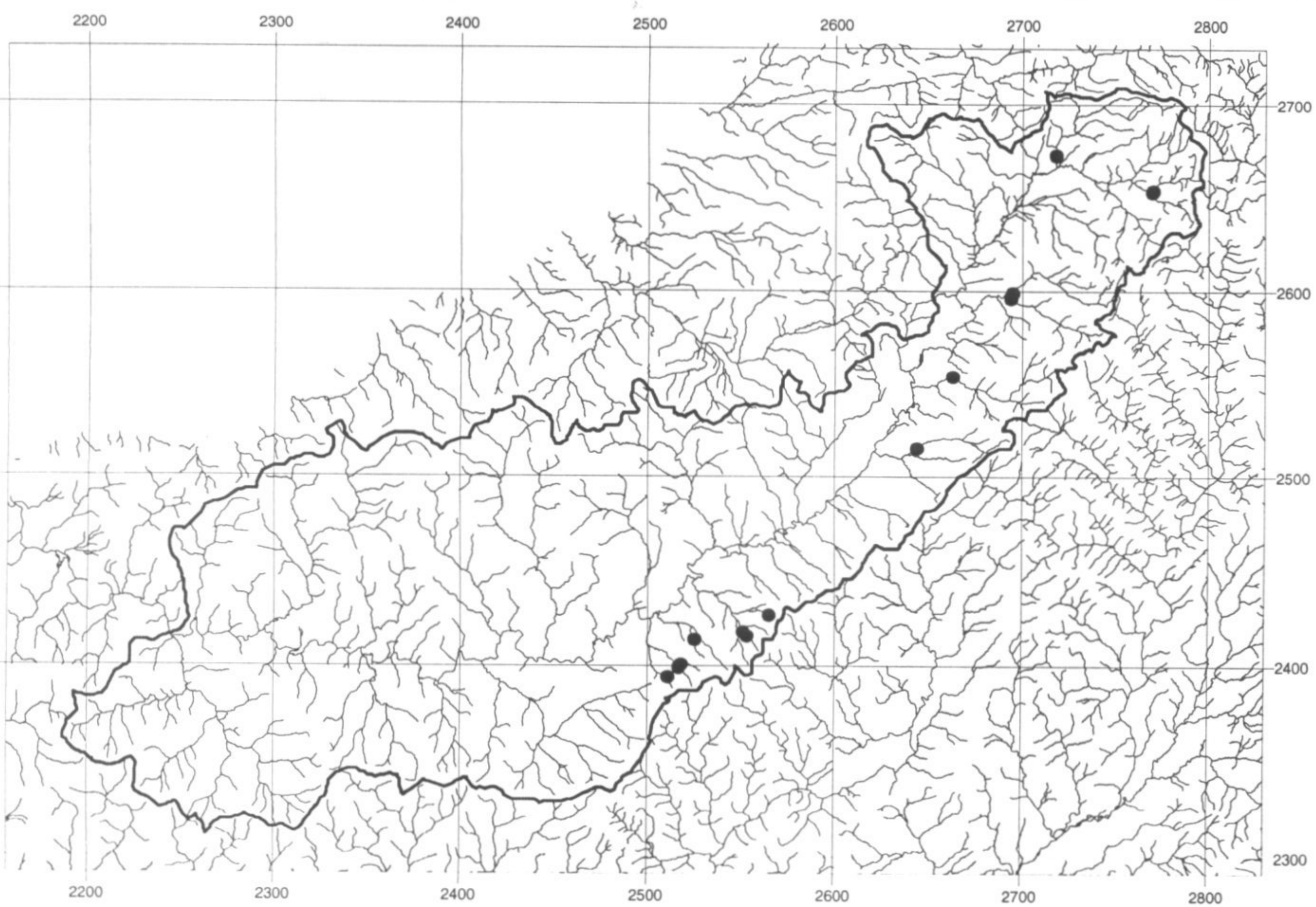
Figure 1

Welsh Acid Waters Survey stream chemistry sampling points

• 102 stream sites in the 1994/95 survey

Catherine Sefton, Institute of Hydrology, 1997

Figure 2



Institute of Hydrology

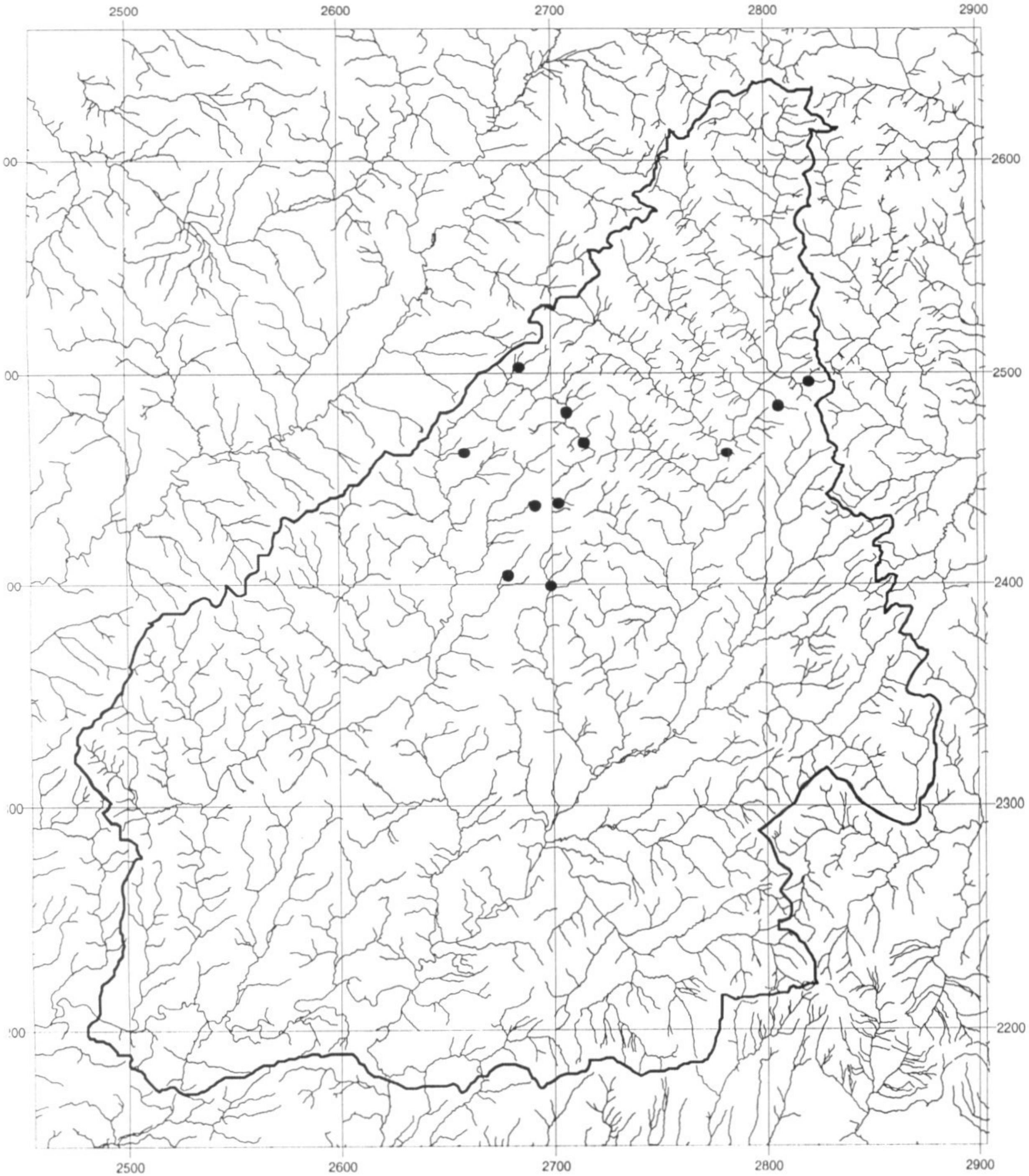
62001 Teifi at Glan Teifi
Acid Waters Sites

Scale 1:400000

1:50000 IH digitised rivers

Map produced at 09:12 on 11 Jul 1997

Figure 3



Institute of Hydrology

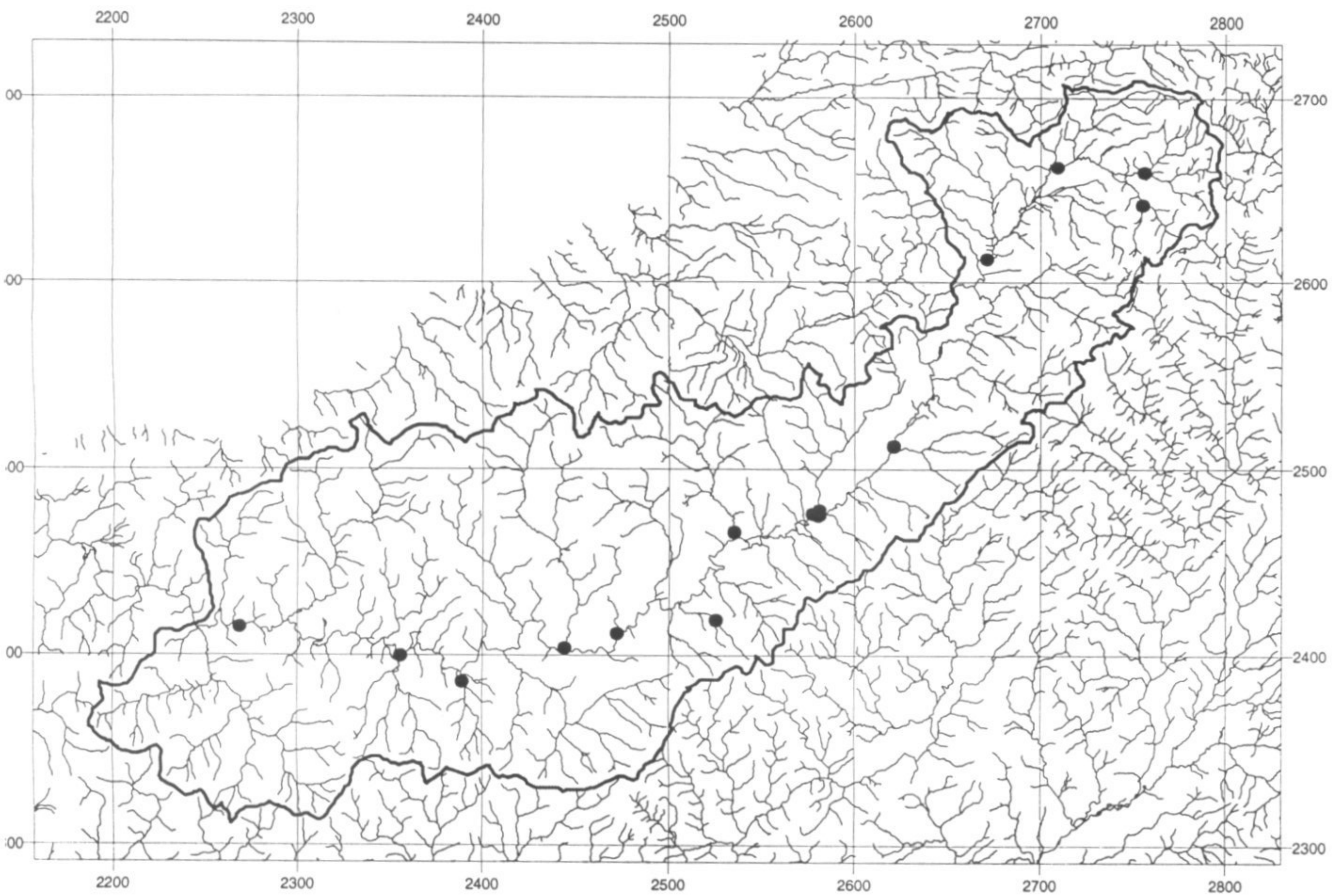
60010 Tywi at Nantgaredig
Acid Waters Sites

Scale 1:300000

1:50000 IH digitised rivers

Map produced at 09:31 on 11 Jul 1997

Figure 4



Institute of Hydrology

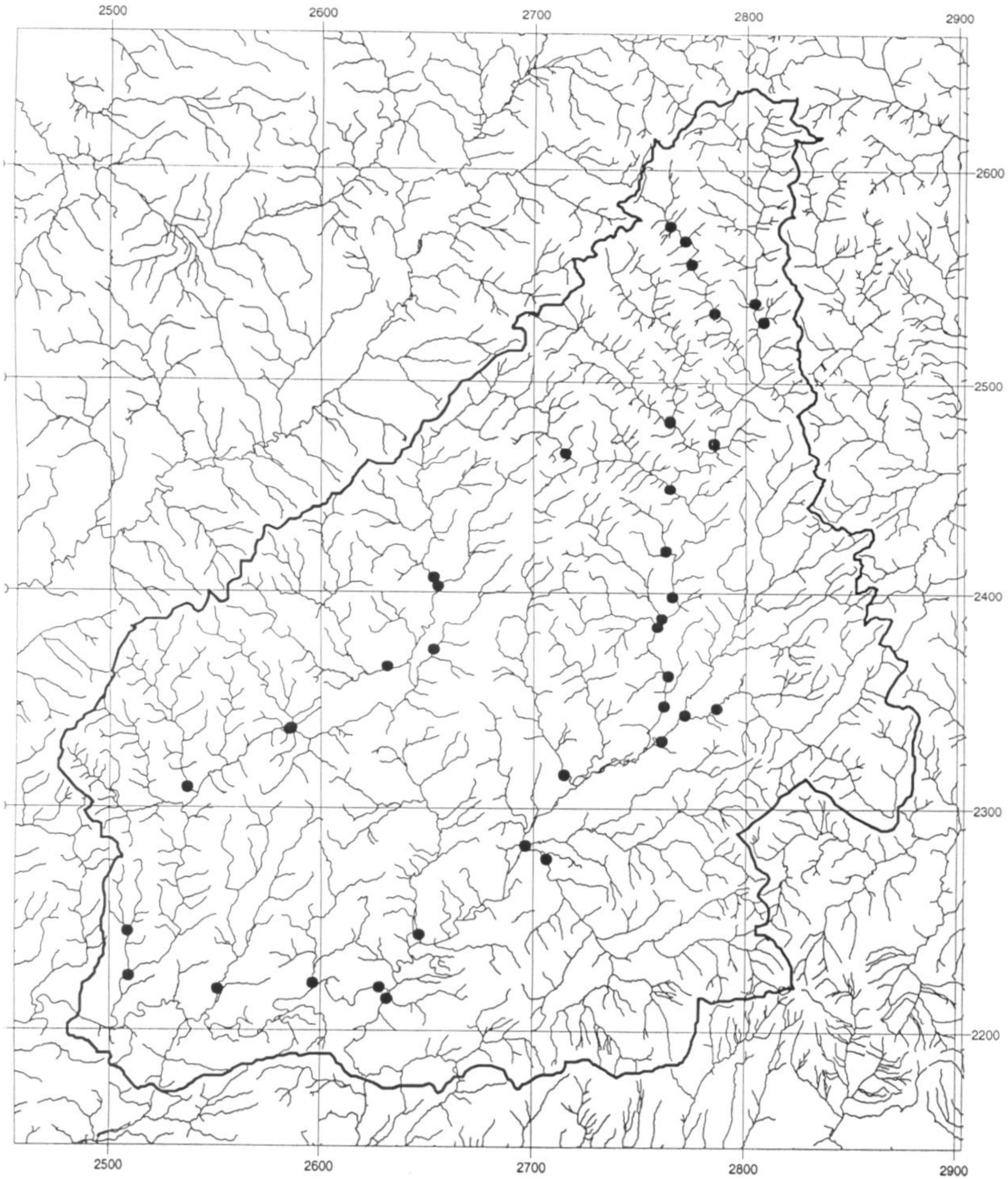
62001 Teifi at Glan Teifi
EA Stream Monitoring Sit

Scale 1:400000

1:50000 IH digitised rivers

Map produced at 13:46 on 27 Jun 1997

Figure 9



Institute of Hydrology

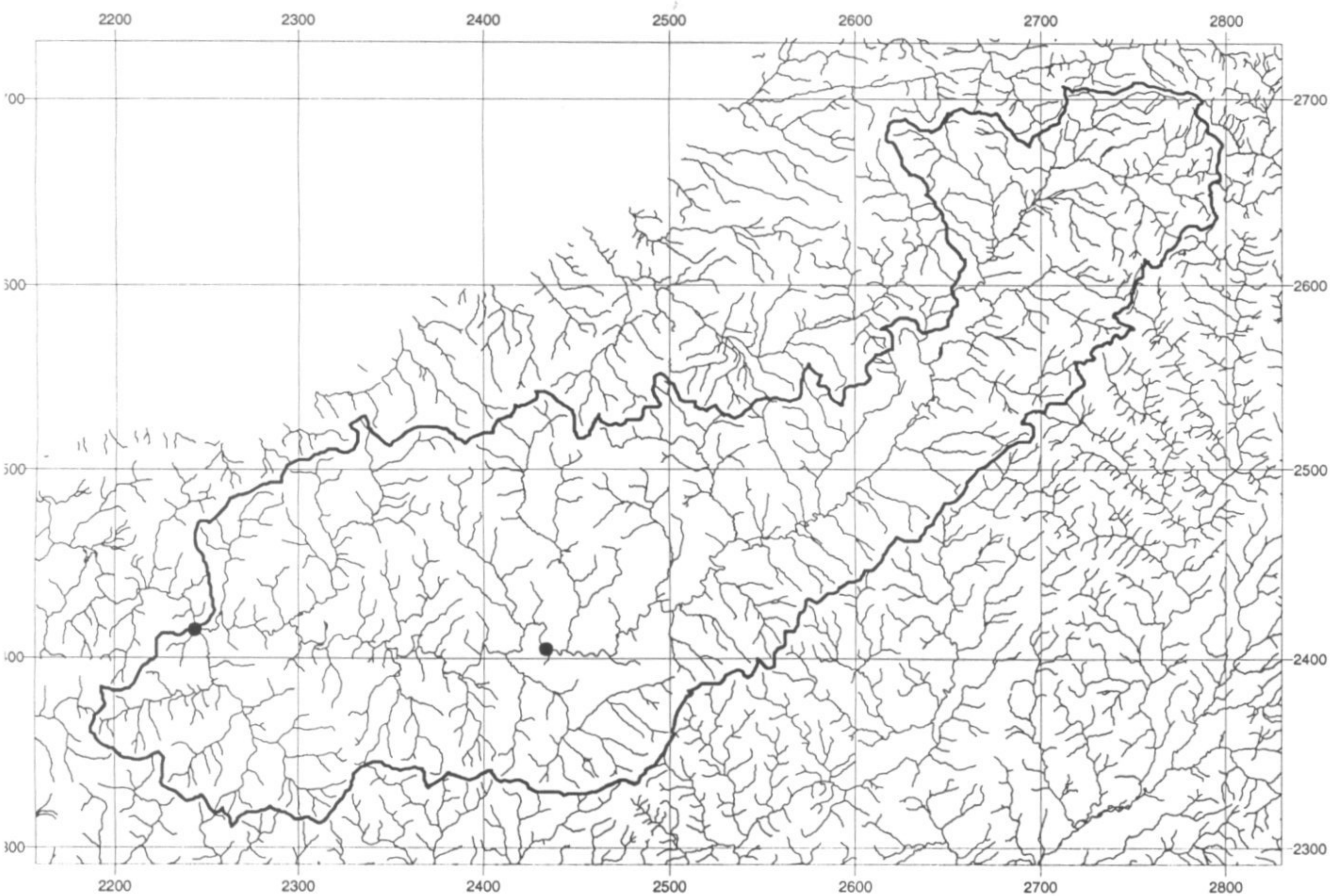
60010 Tywi at Nantgaredig
EA Stream Monitoring Site

Scale 1:300000

1:50000 IH digitised rivers

Map produced at 11:58 on 27 Jun 1997

Figure 6



Institute of Hydrology

62001 Teifi at Glan Teifi
River Gauging Sites

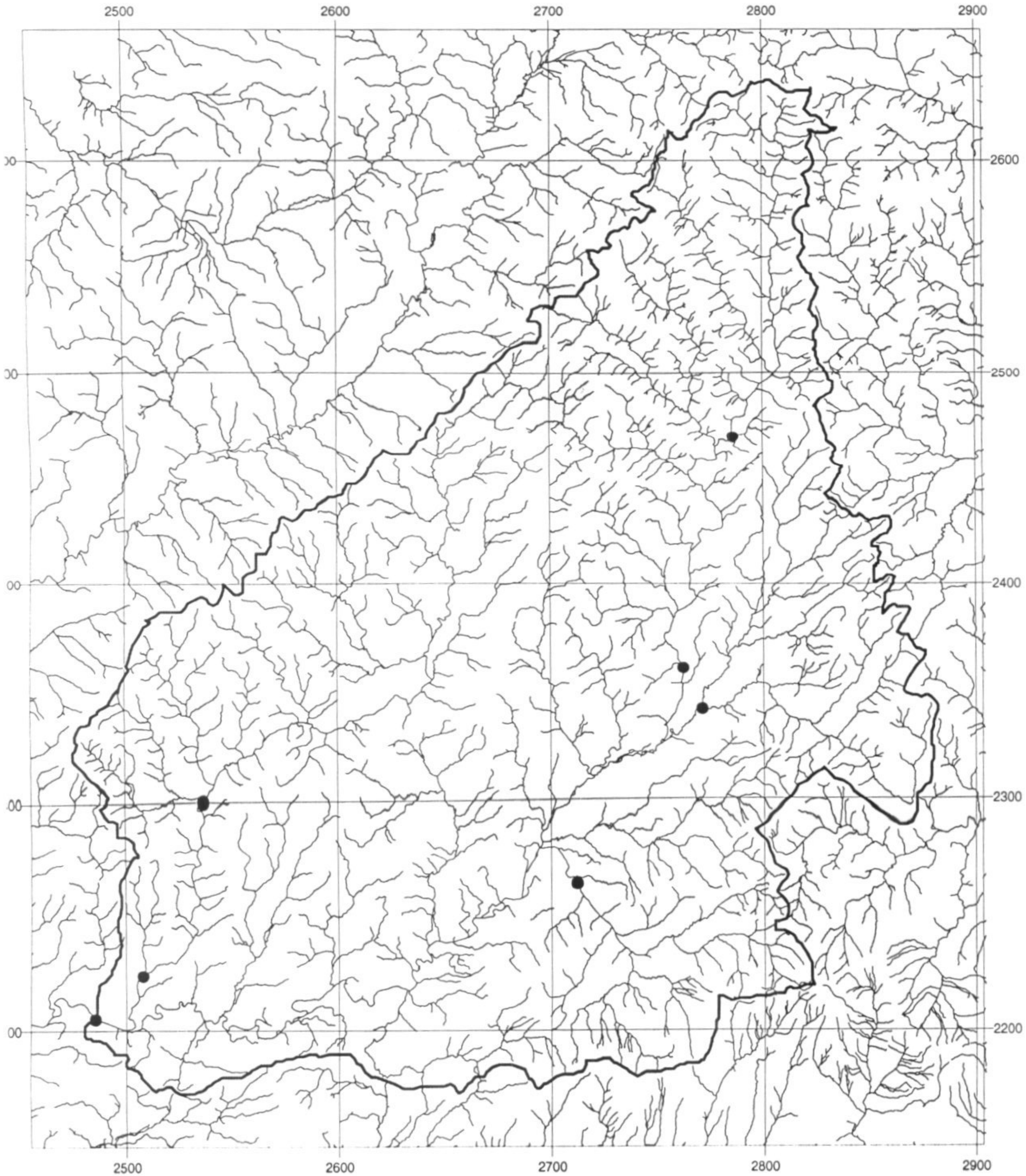
Scale 1:400000

KEY

1:50000 IH digitised rivers

Map produced at 09:53 on 14 Jul 1997

Figure 7



Institute of Hydrology

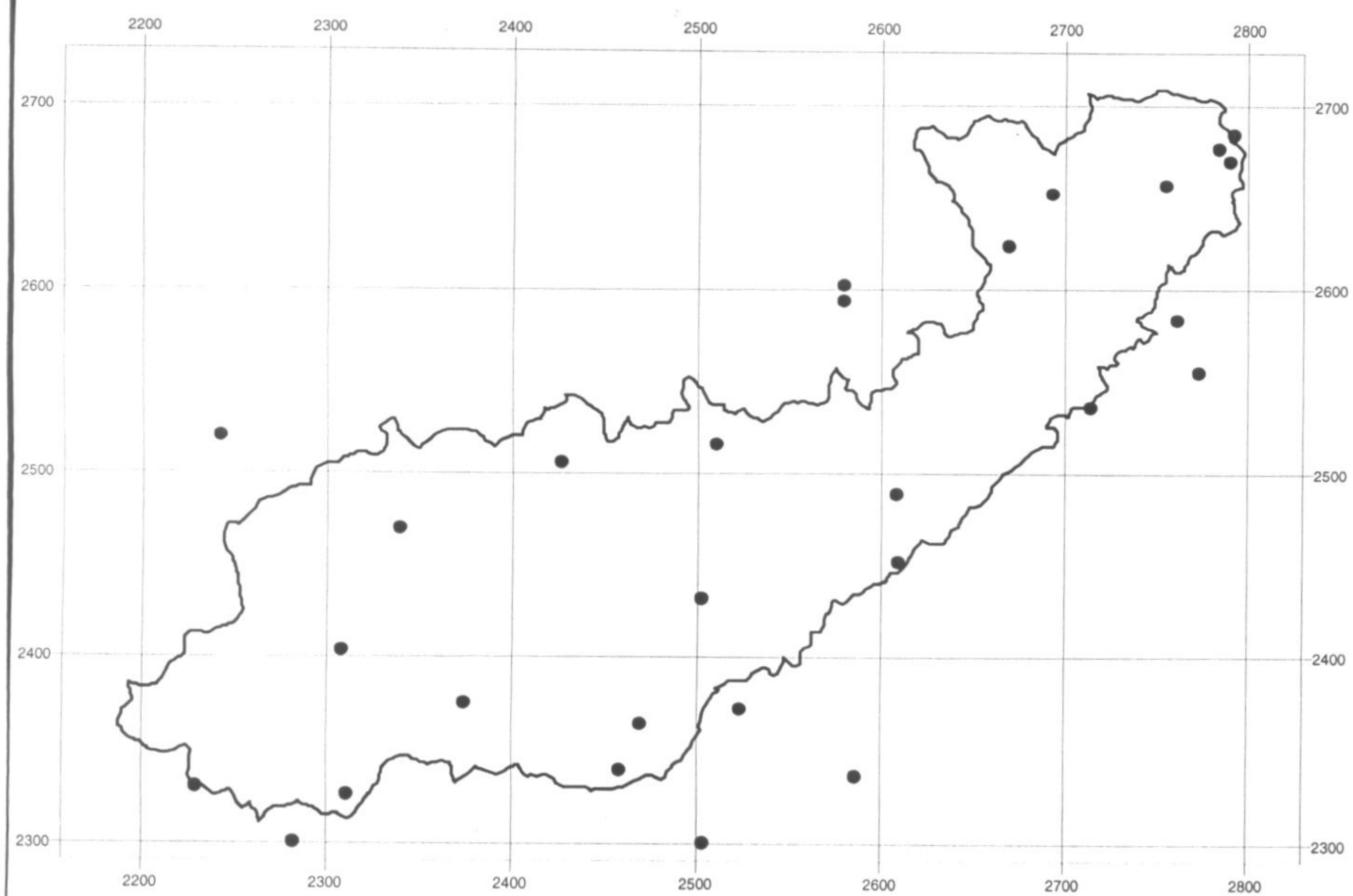
60010 Tywi at Nantgaredig
River Gauging Sites

Scale 1:300000

1:50000 IH digitised rivers

Map produced at 09:42 on 14 Jul 1997

Figure 8



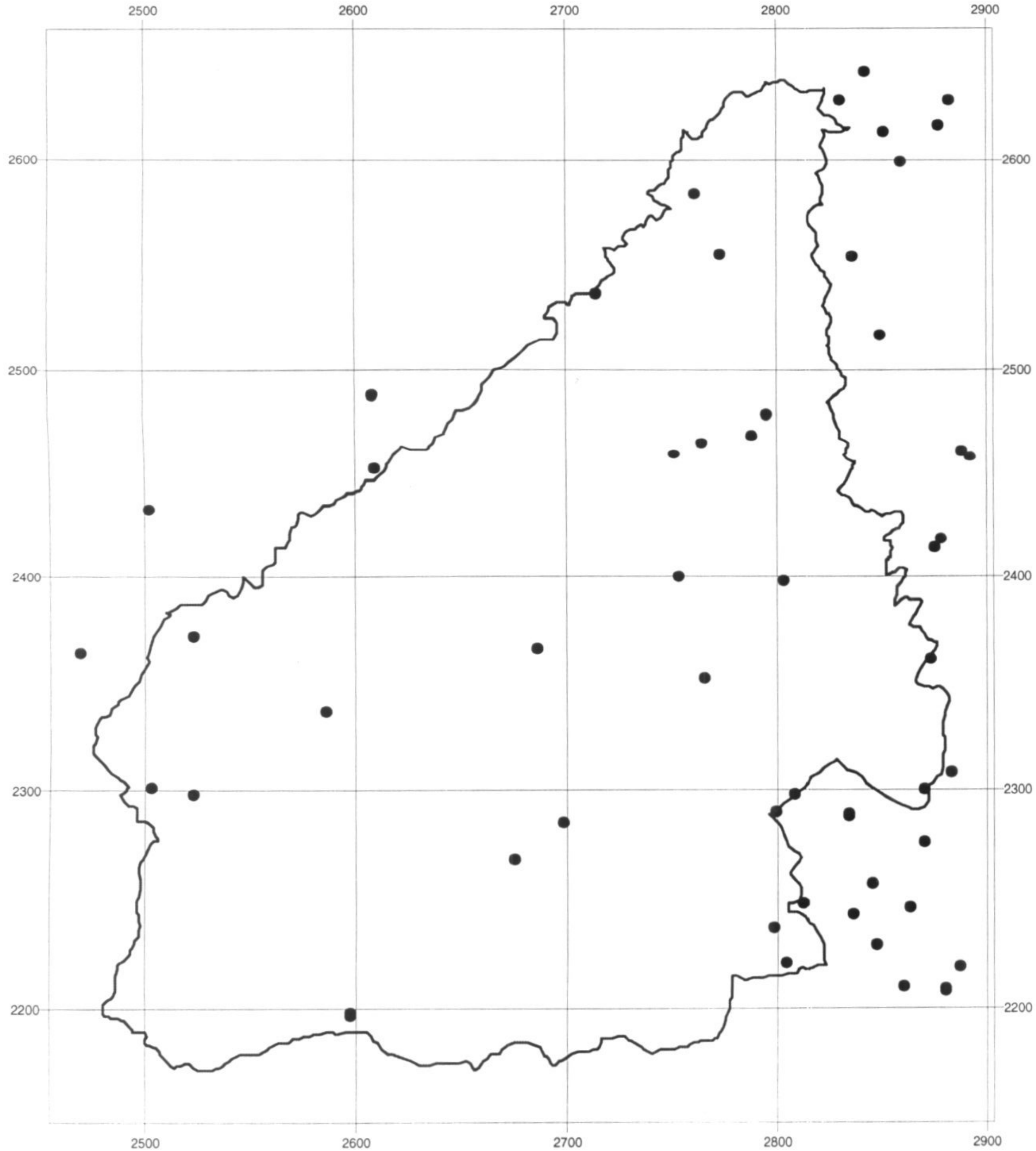
Institute of Hydrology

62001 Teifi at Glan Teifi
Rainfall Gauges

Scale 1:400000

Map produced at 15:15 on 14 Jul 1997

Figure 9



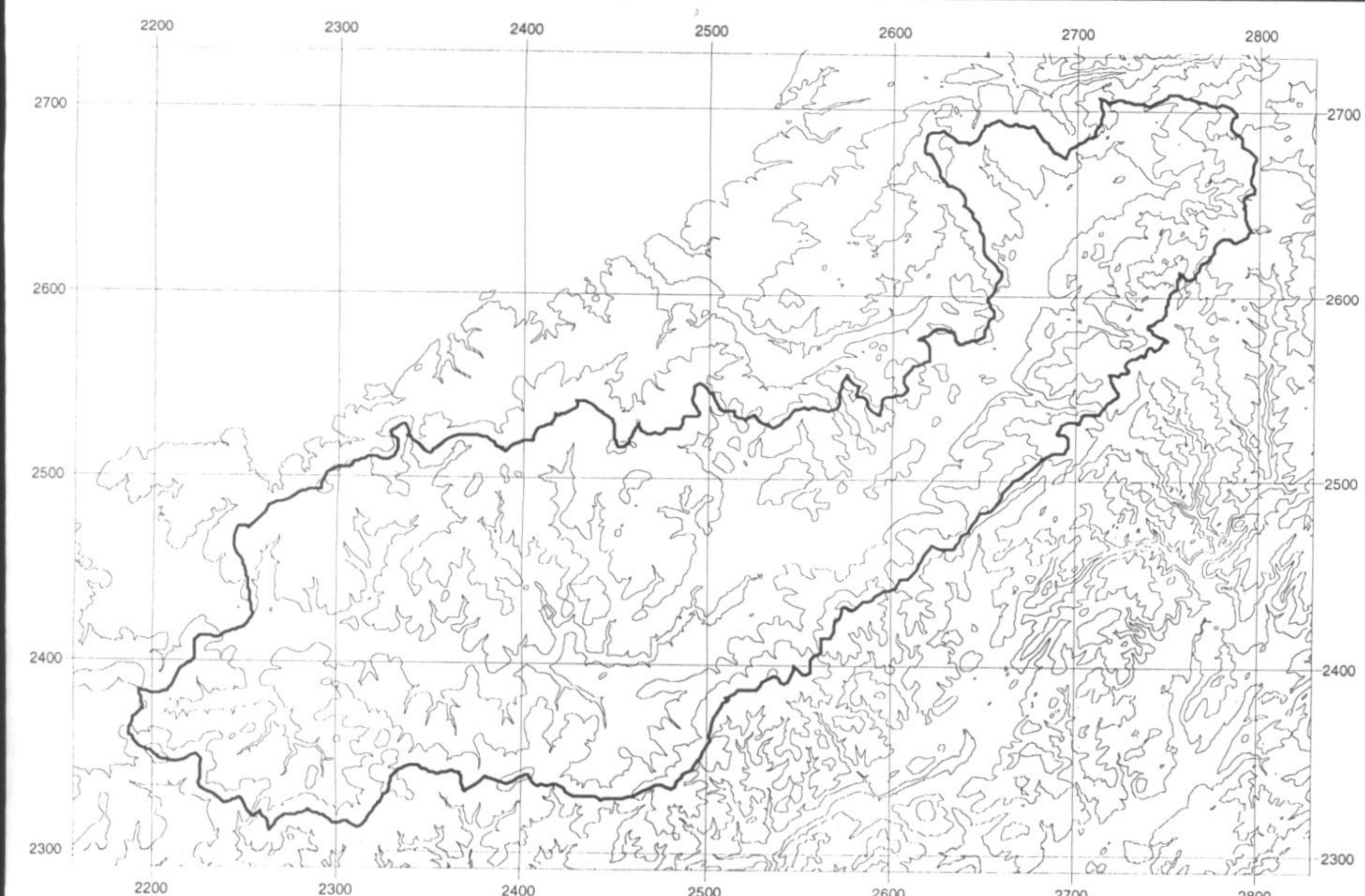
Institute of Hydrology

60010 Tywi at Nantgaredig
Rainfall Gauges

Scale 1:300000

Map produced at 15:23 on 23 Sep 1997

Figure 10



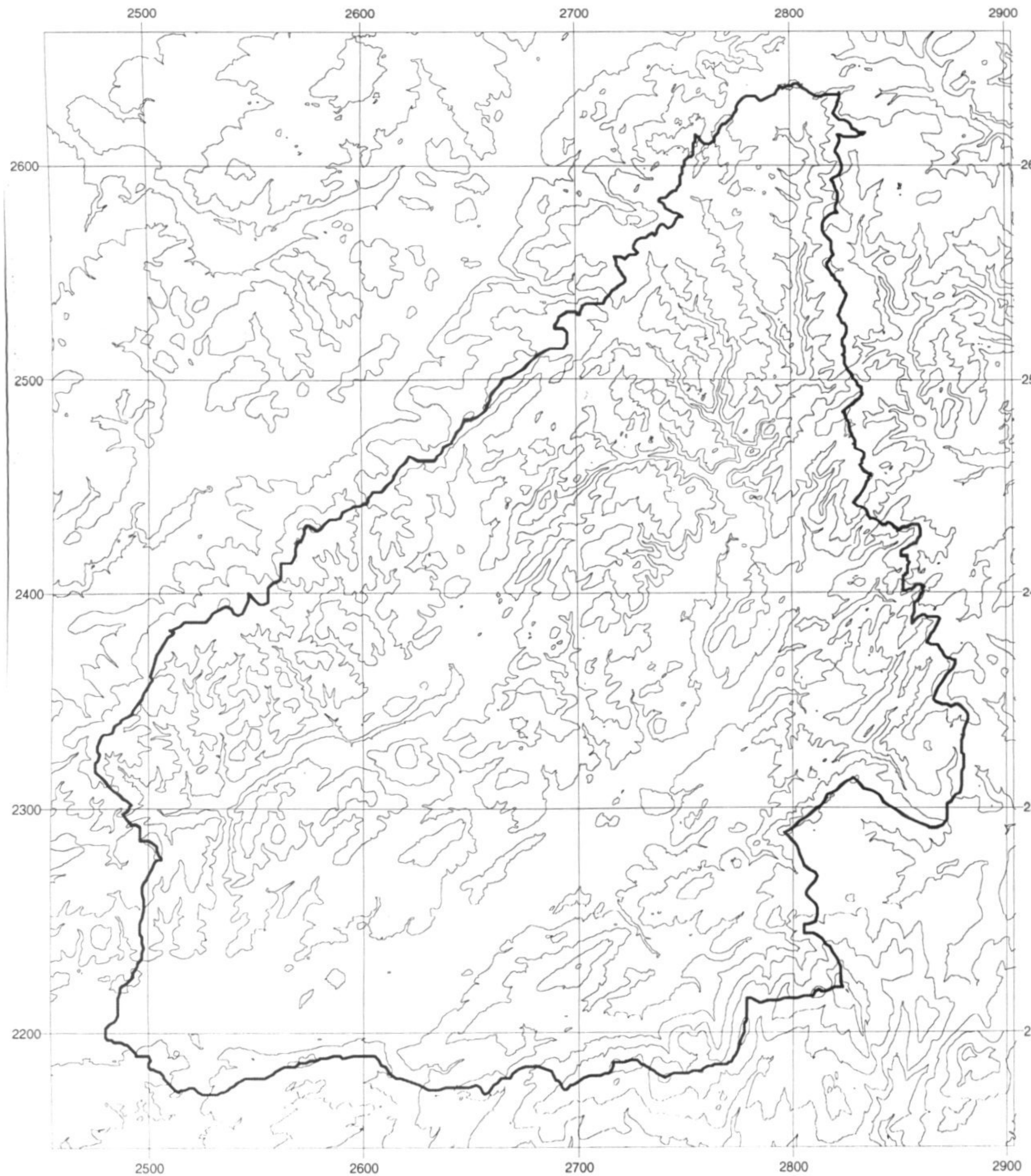
Institute of Hydrology

62001 Teifi at Glan Teifi
Contours at 100m interval

Scale 1:400000

Ordnance Survey 1:50000 contours

Map produced at 09:44 on 18 Jul 1997



Institute of Hydrology

60010 Tywi at Nantgaredig
Contours at 100m interval

Scale 1:300000

———— Ordnance Survey 1:50000 contours

Map produced at 15:36 on 23 Sep 1997

Figure 12

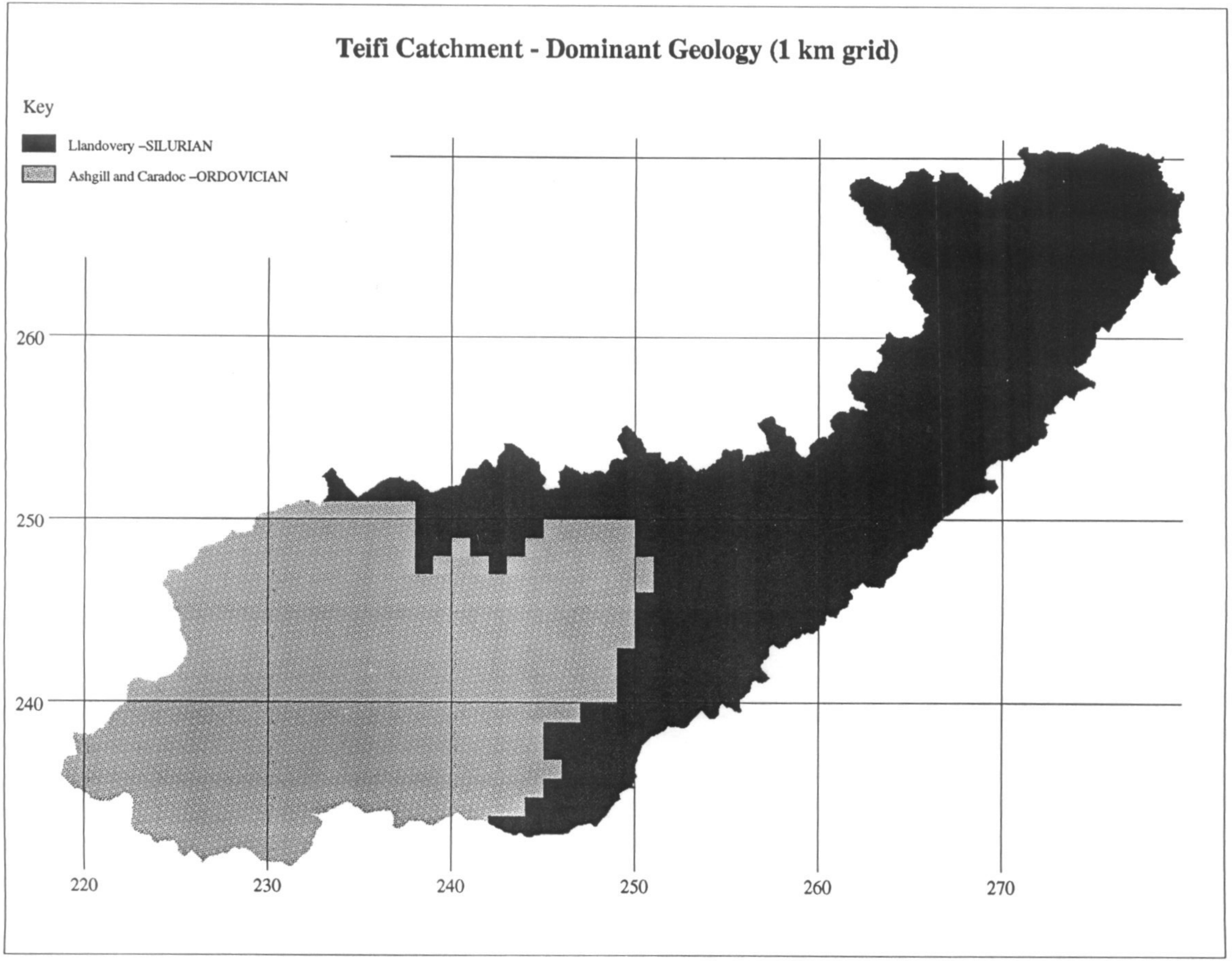
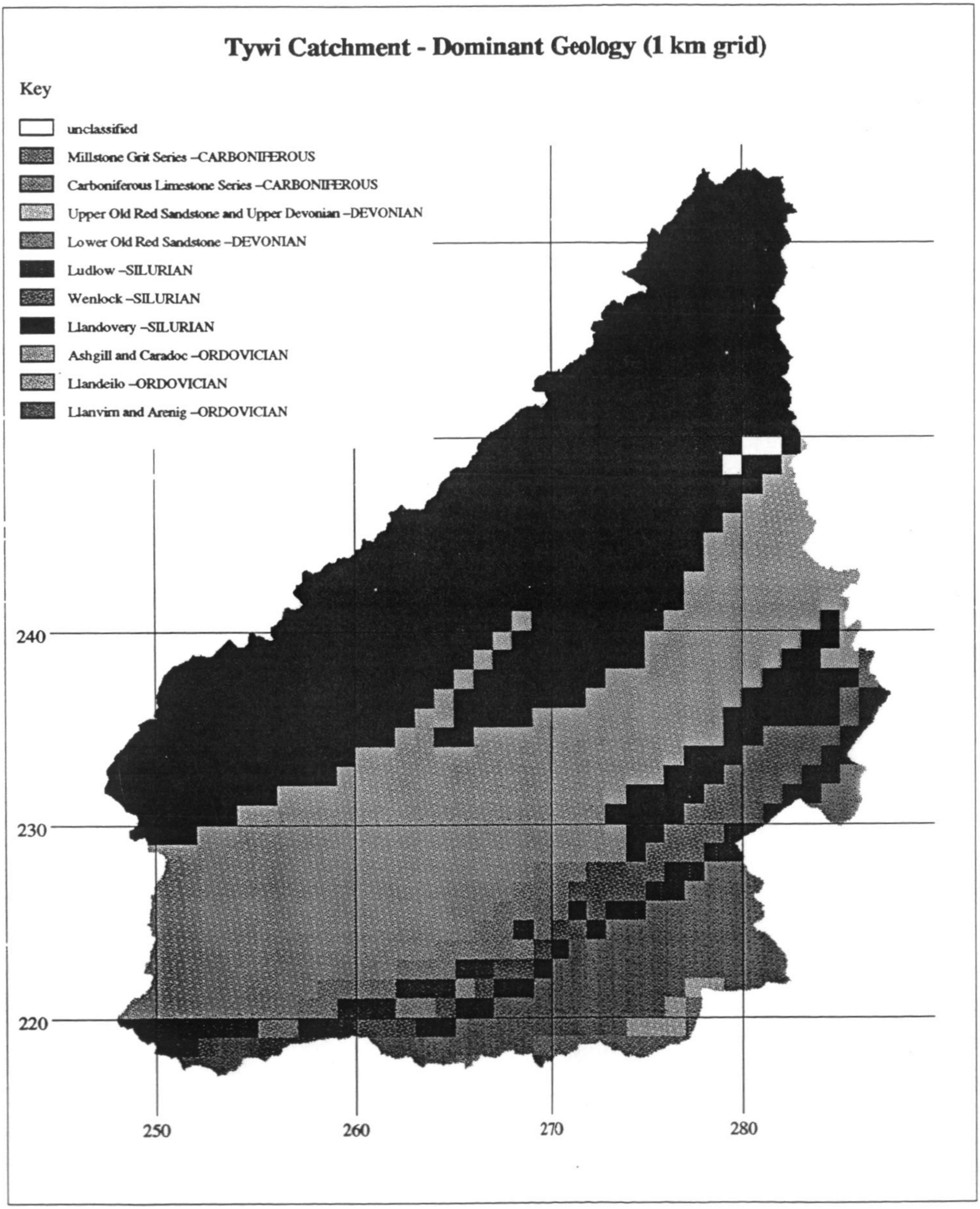
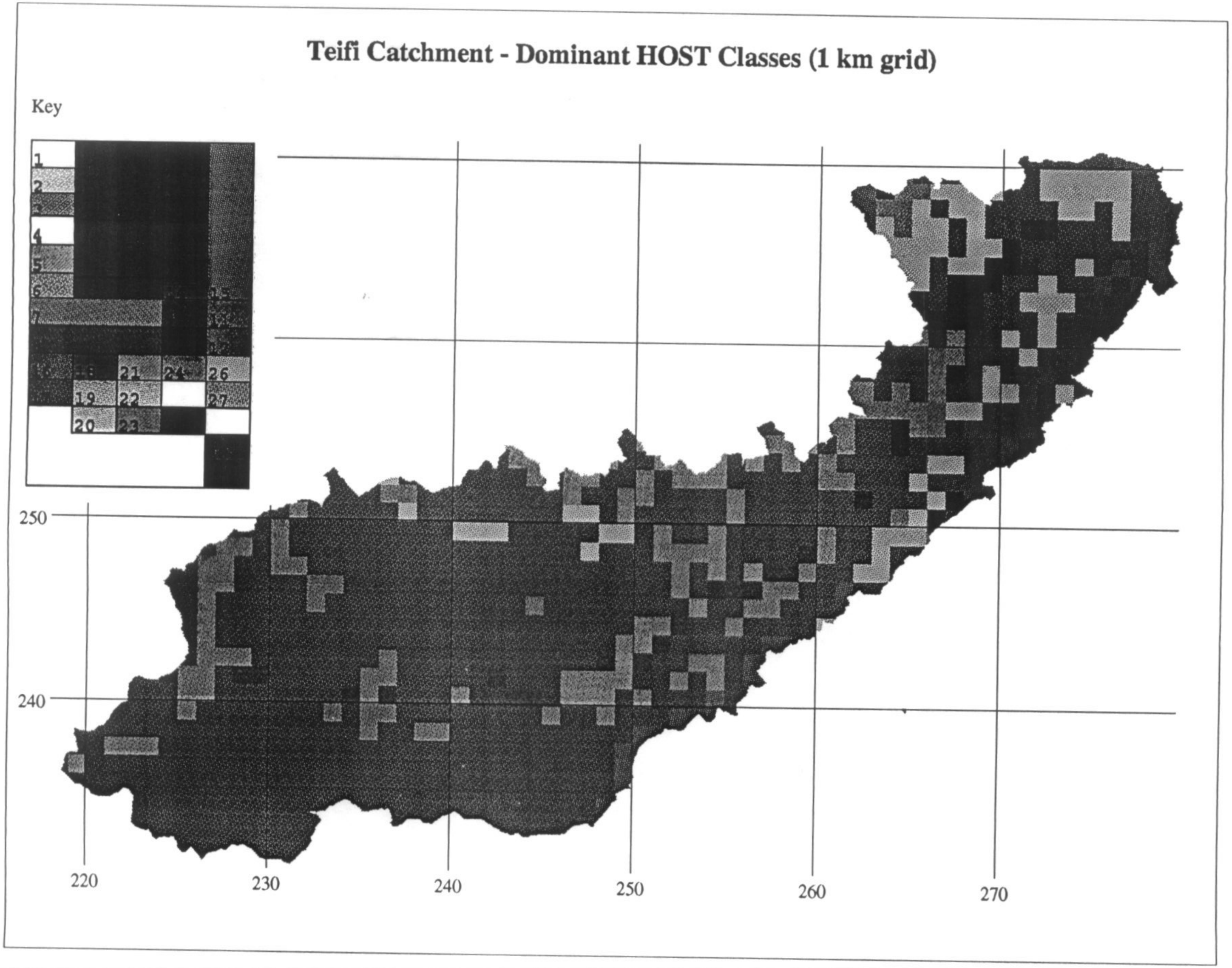

Teifi Catchment - Dominant Geology (1 km grid)
Key
Llandovery –SILURIAN
Ashgill and Caradoc –ORDOVICIAN
260
250
240
220
230
240
250
260
270

Figure 13



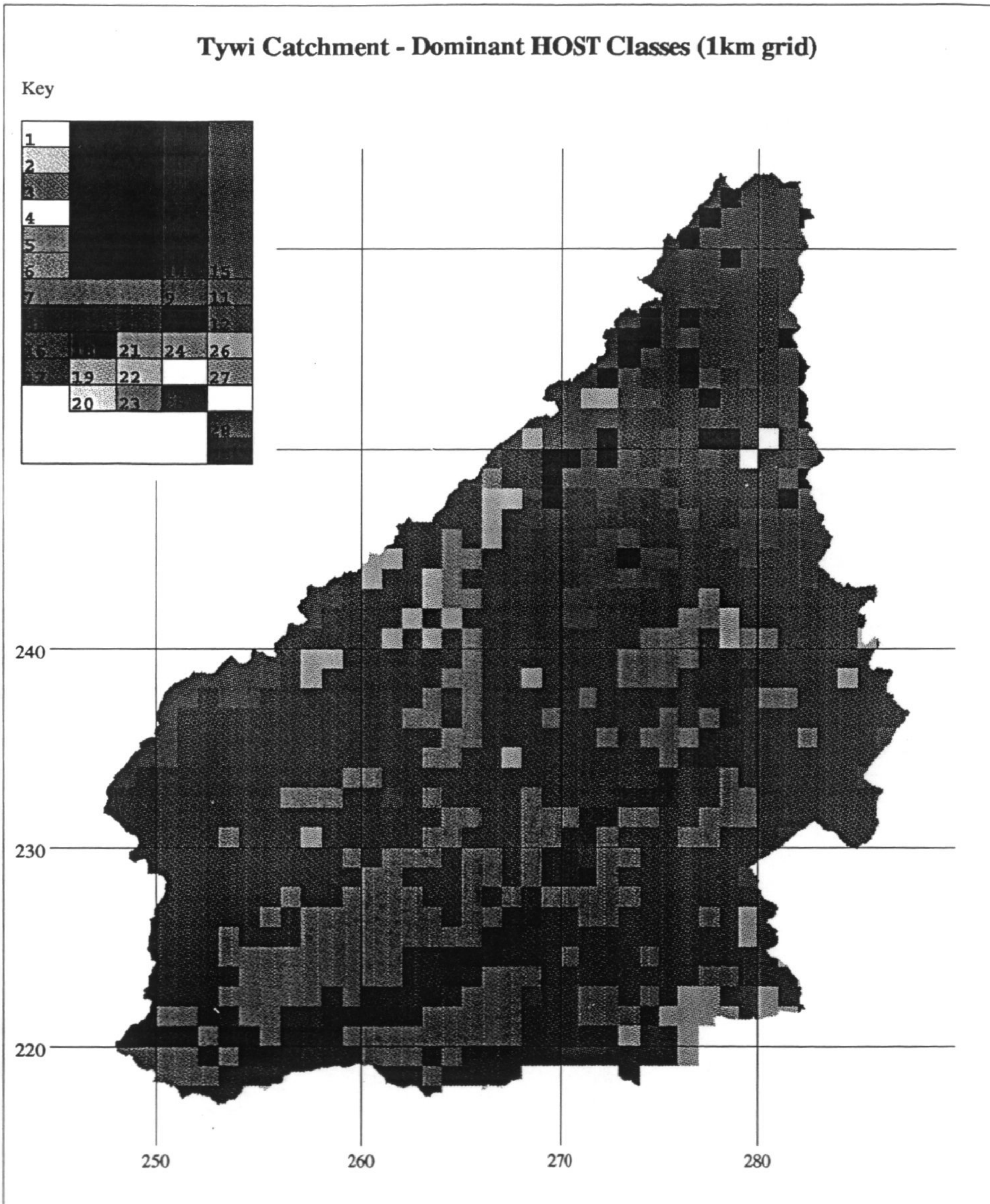
Tywi Catchment - Dominant Geology (1 km grid)
Key
unclassified
Millstone Grit Series –CARBONIFEROUS
Carboniferous Limestone Series –CARBONIFEROUS
Upper Old Red Sandstone and Upper Devonian –DEVONIAN
Lower Old Red Sandstone –DEVONIAN
Ludlow –SILURIAN
Wenlock –SILURIAN
Llandovery –SILURIAN
Ashgill and Caradoc –ORDOVICIAN
Llandeilo –ORDOVICIAN
Llanvirn and Arenig –ORDOVICIAN
240
230
220
250
260
270
280

Figure 14



Teifi Catchment - Dominant HOST Classes (1 km grid)
Key
1
2
4
5
6
7
18
19
20
21
22
23
24
26
27
250
240
220
230
240
250
260
270

Figure 15



Tywi Catchment - Dominant HOST Classes (1km grid)
Key
1
2
3
4
5
6
7
9
11
12
15
16
18
19
20
21
22
23
24
26
27
28
240
230
220
250
260
270
280

Figure 16

62001 Teifi at Glan Teifi

Acid Waters Subcatchments

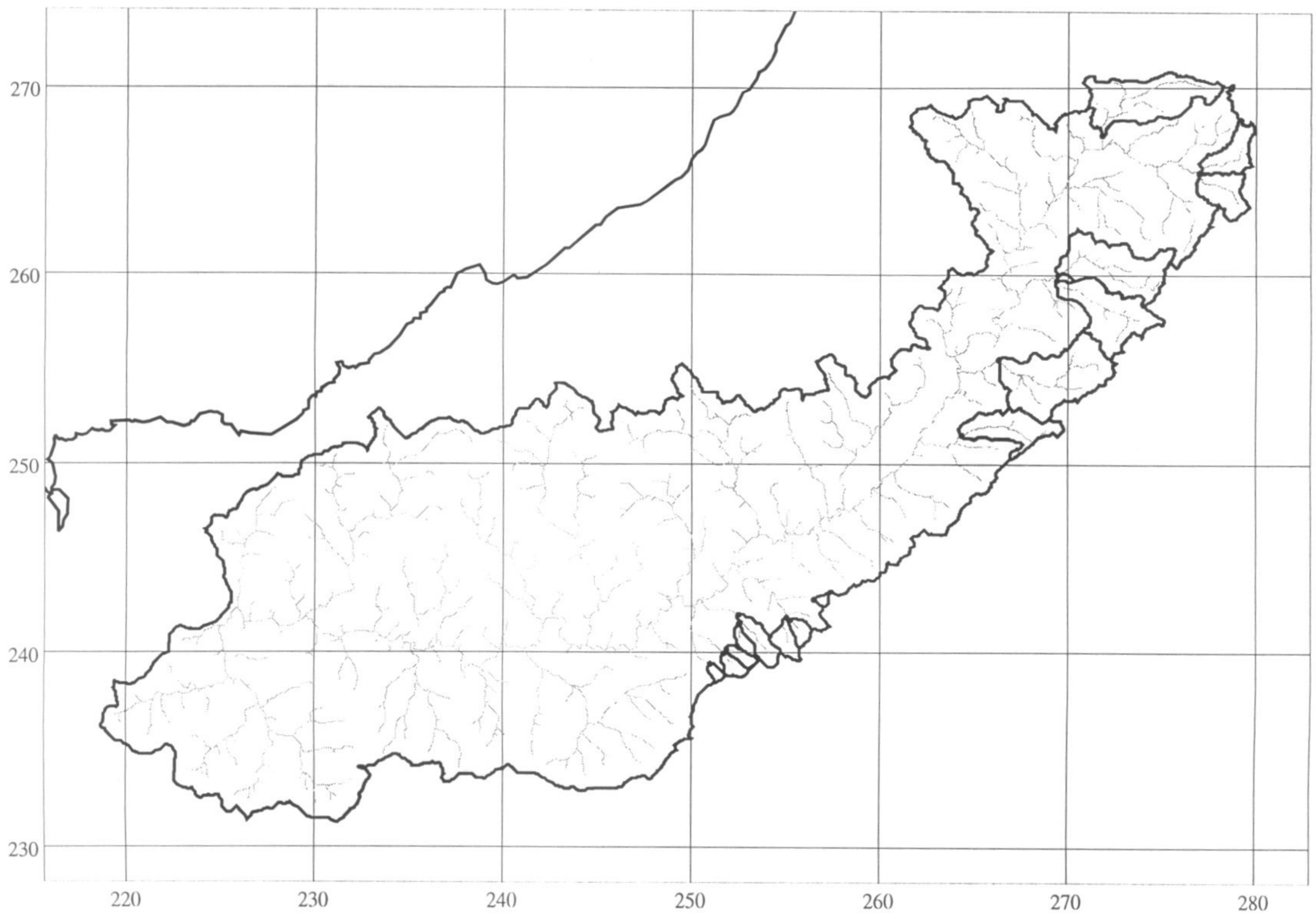


Figure 17

60010 Tywi at Nantgaredig

Acid Waters Subcatchments

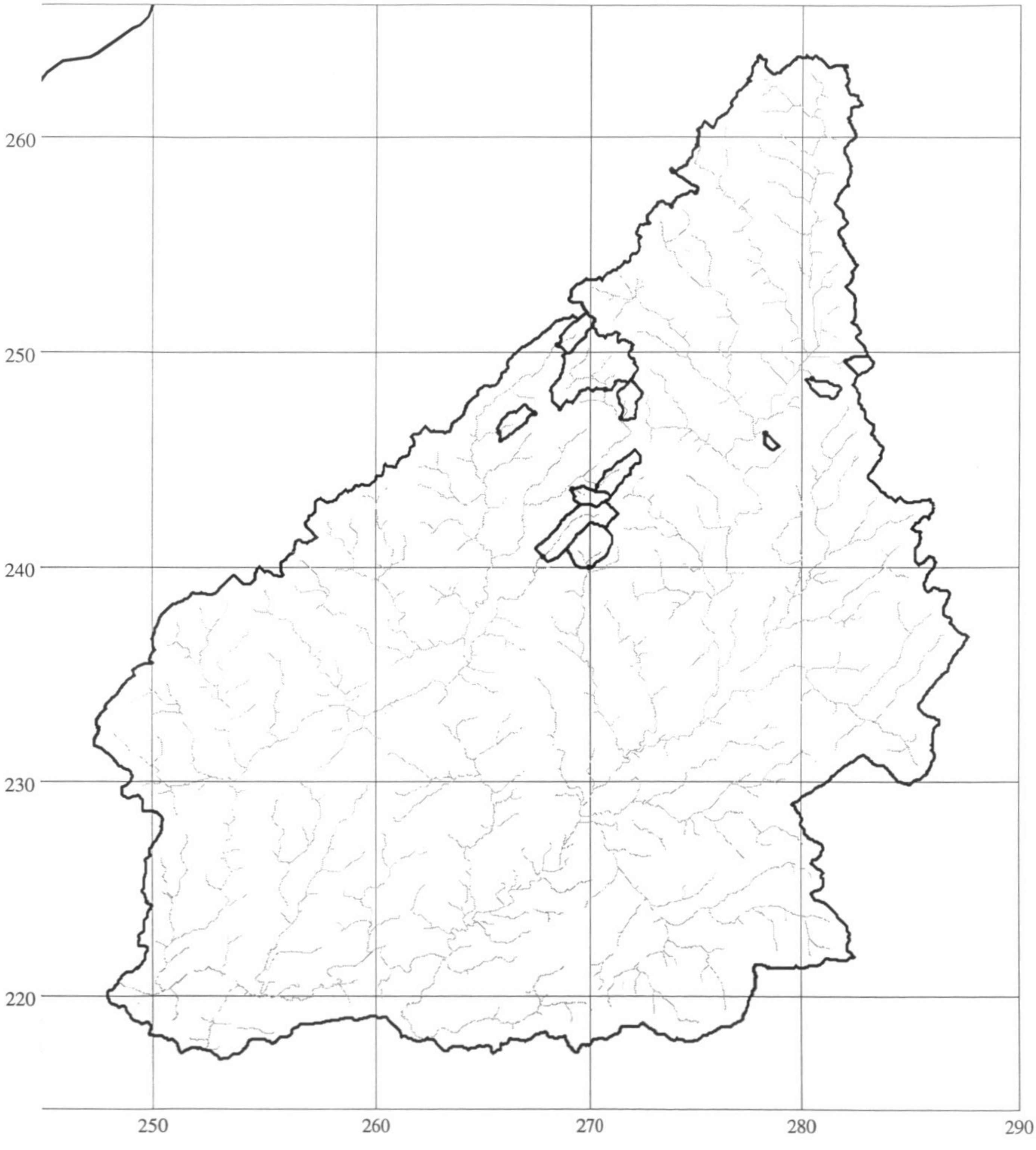


Figure 18

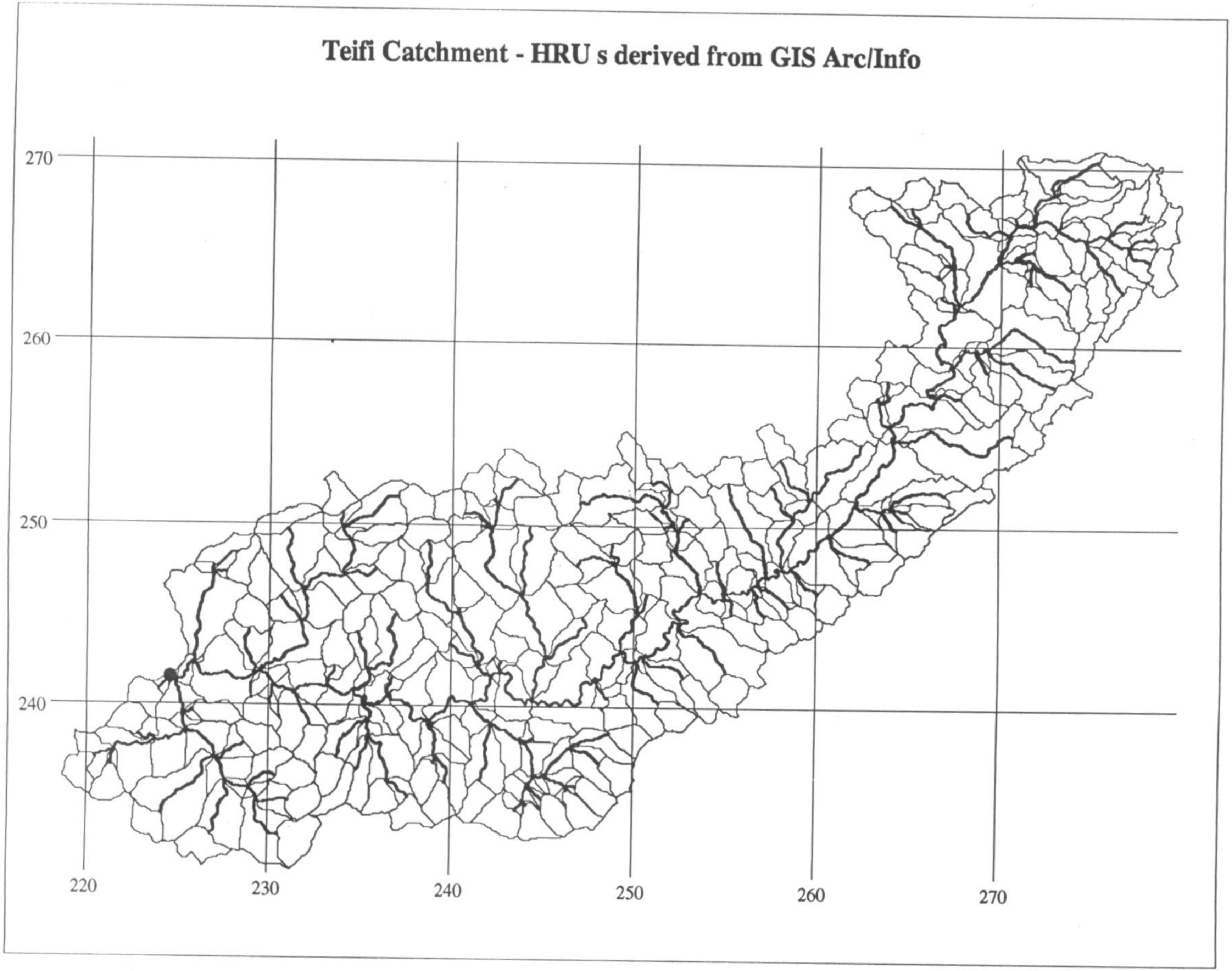

Teifi Catchment - HRU s derived from GIS Arc/Info
270
260
250
240
220
230
240
250
260
270

Figure 19

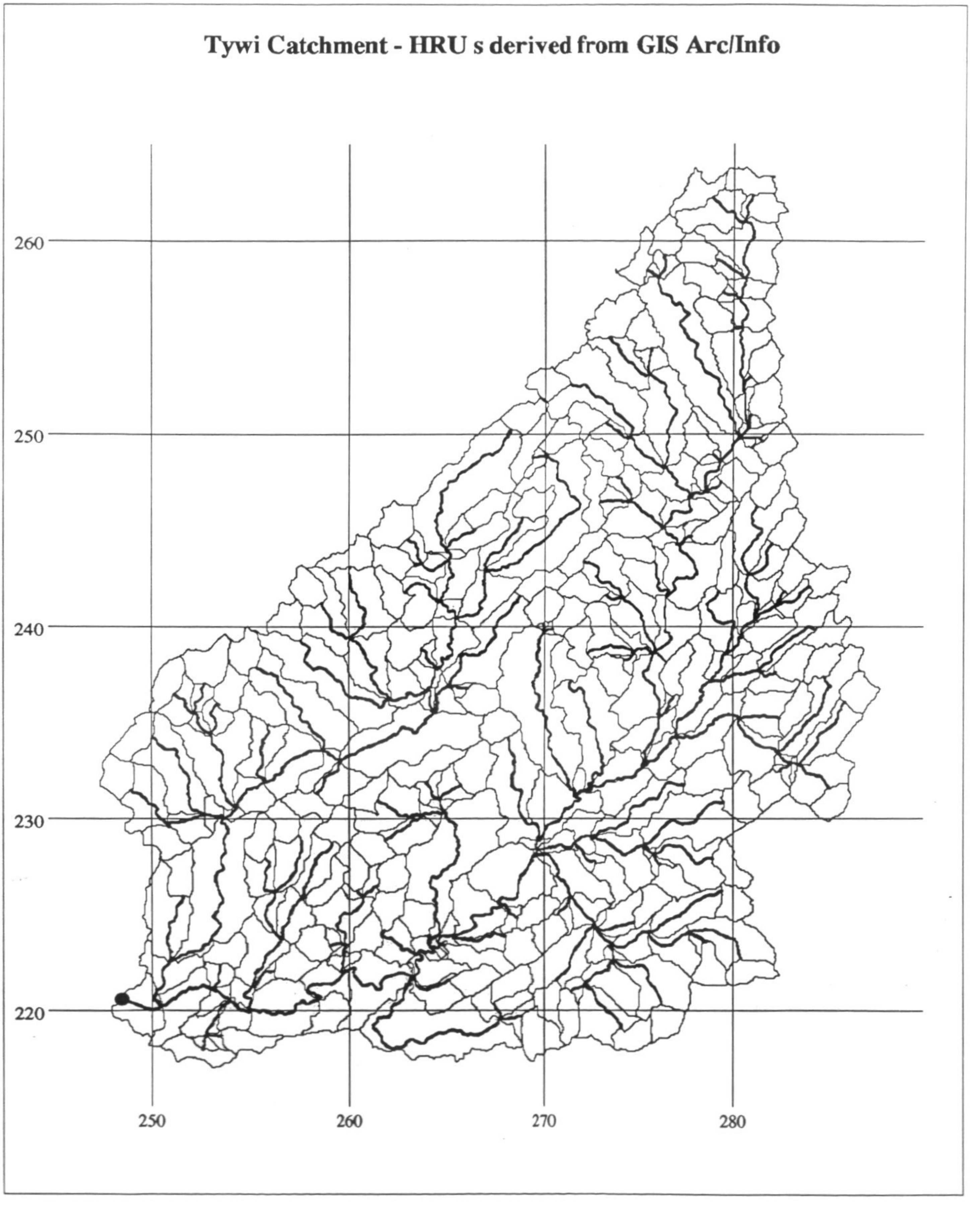
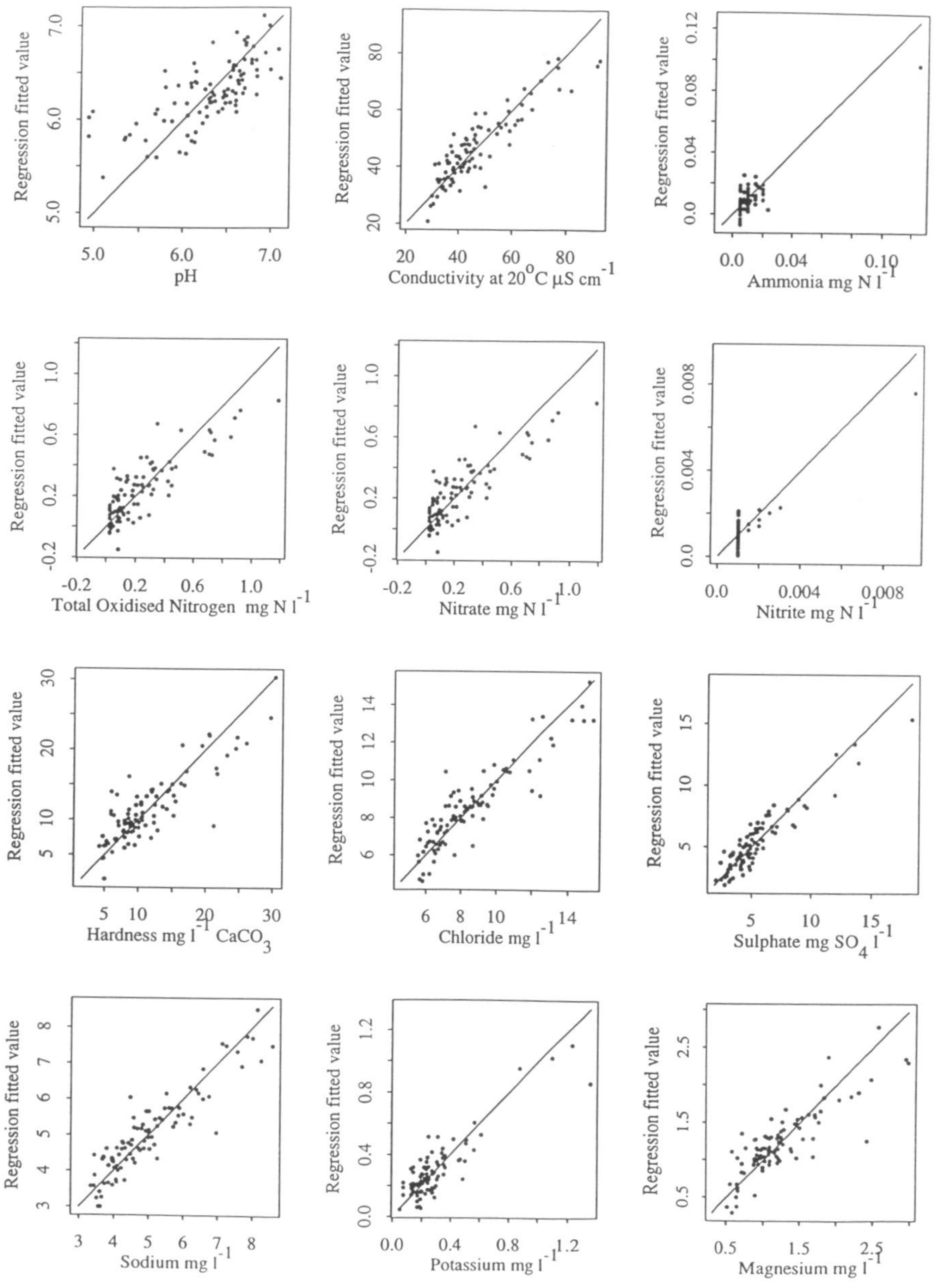

Tywi Catchment - HRU s derived from GIS Arc/Info
260
250
240
230
220
250
260
270
280

Figure 20

Welsh Acid Waters Survey 1994-95

Stepwise regression of contaminant concentration on restricted combined data



Welsh Acid Waters Survey 1994-95

Stepwise regression of contaminant concentration on restricted combined data

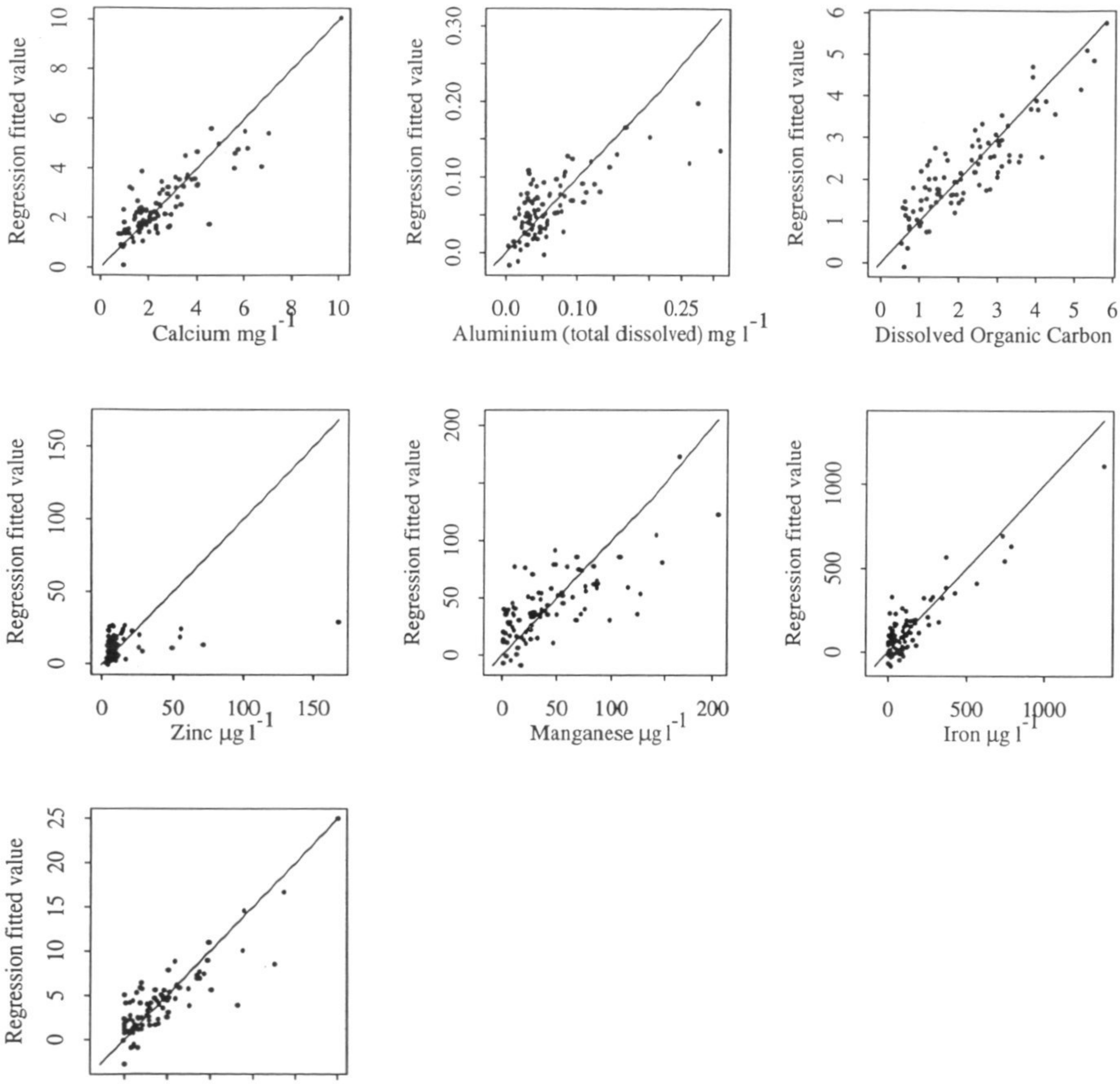


Figure 21 Predicted vs Observed Base Cation Streamflow Chemistry

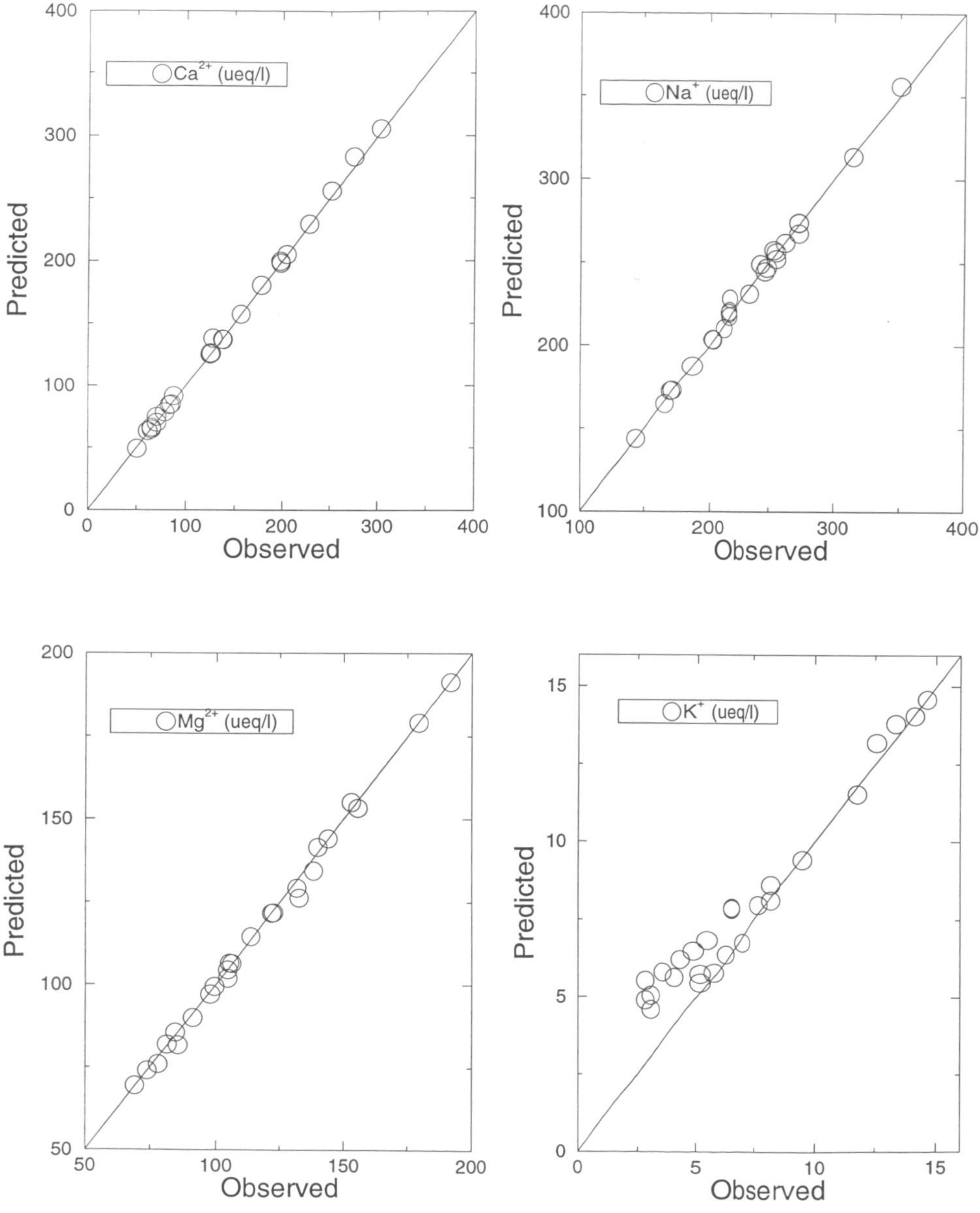


Figure 22 Predicted vs Observed Anion Streamflow Chemistry and Percentage Base Saturation

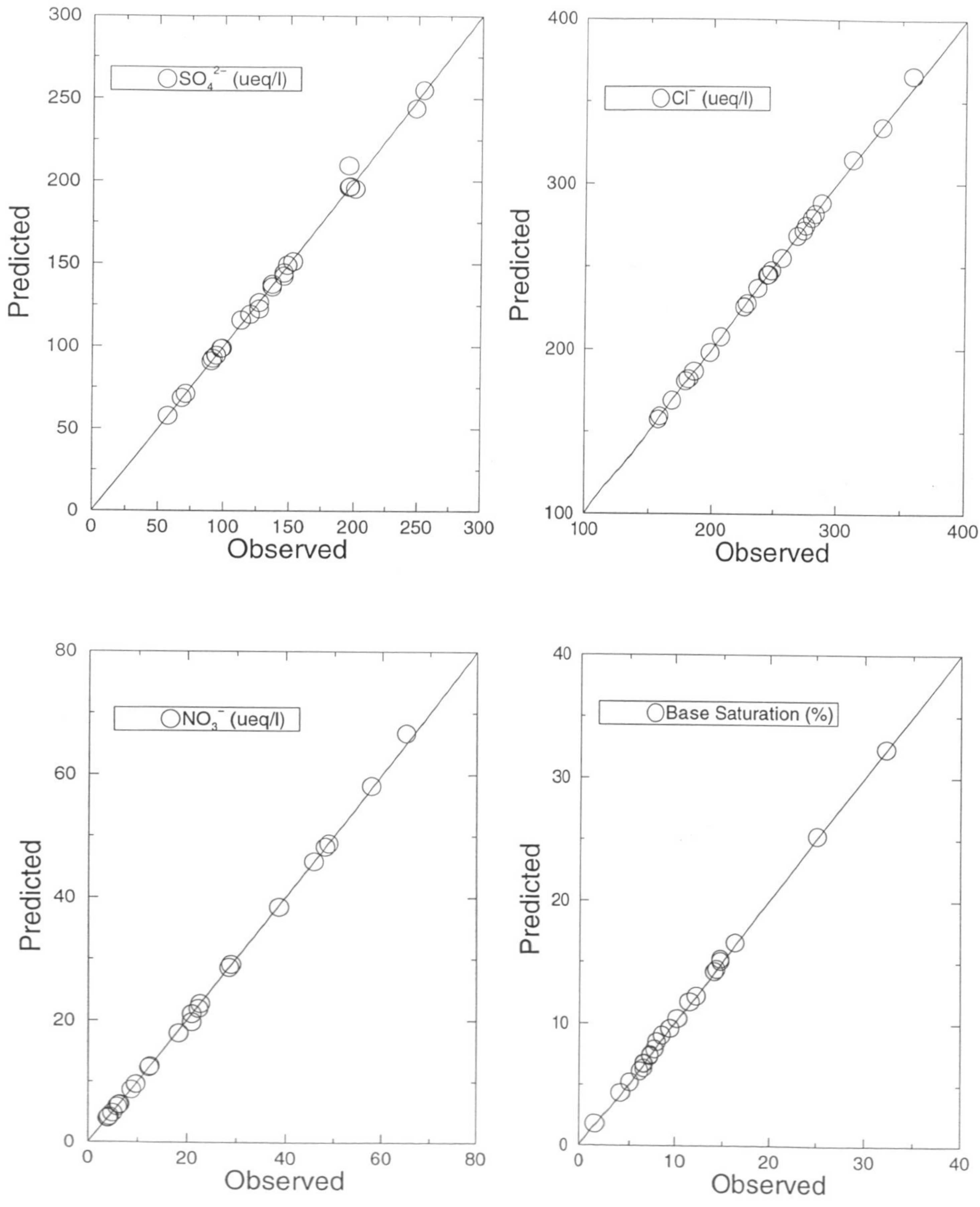


Figure 23 Predicted vs Observed Streamflow ANC, pH and the sum of base cations, and the relationship between pH and ANC.