## Craig Goch Report No. 11

## The behaviour and budgets of selected ions in the Wye Catchment

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### Introduction

The river Wye, 250 km long and draining a predominantly rural catchment of 4183 km<sup>2</sup>, rises in mid-Wales (677m O.D.) and flows to the Severn Estuary (Fig 1).

Samples for chemical analysis were obtained from sites 1 to 14 at two-week intervals over the period April 1975 to July 1976 and from site 15 at weekly intervals from 1973.

### <u>Results</u>

1. Calcium. Mean calcium concentrations increase from 1mg/l in the upper catchment to 32 mg/l downstream (Fig 2) reflecting changes in the geology of the catchment (Fig 1). Several aquatic invertebrates, e.g. *Sphaerium corneum, Gammarus pulex, Asellus aquaticus,* were restricted to sites with mean concentrations greater than 10mg/l. *Ancylus fluviatilis* was more widely distributed but was not recorded at site 1 (mean concentration : 2.4mg/l. The significance of calcium in relation to the distribution of molluscs and crustaceans has been discussed by several authors (see Macan, 1950; Maitland, 1966; Reynoldson, 1961) but other environmental factors are clearly also important.

At all gauged sites except site 1C, calcium concentrations (*[Ca]*) were significantly related to flow (F) according to the equation

Log [Ca] = a + b log F

a and b being constants. At these sites *[Ca]* was reduced by increasing flow, the greatest dilution effect being in the lower catchment (Table 1). *[Ca]*-flow relationships very widely with rainfall, land-use, topography and geology (Depentris, 1976; Edwards, 1973).

2. Silicon (as reactive silica  $-SiO_2$ ). Annual rhythms recorded at site 15 showed high winter concentrations (6mg SiO<sub>2</sub>/I) and low spring and summer ones (<0.5mg/I). Concentrations of silicon and chlorophyll <u>a</u> at site 15 were inversely correlated during the period of study (r = -0.39: p<0.01) silicon depletion resulting, in part, from diatom production.

For the period April 1975 – July 1976, whilst in the headwaters the silicon concentration decreases with increasing flow, the relationship becomes progressively reversed downstream with concentrations in the lower catchment being markedly higher at high flows (Table 1). This behaviour probably reflects uptake of silicon by dietoms in the spring and summer months when lower flows, providing maximum retention time and contact opportunity with the

benthos, generally occur. The relationship between silicon concentration and flow at the downstream site (site 15) (Table 1) during the period of minimal diatom growth (Nov – Feb) is similar to that at the upstream site (site 1) throughout the year with high concentrations at low flows, supporting the conclusion that silicon removal associated with diatom growth is significant.

The maximum concentration of  $SiO_2$  at high flows increases from 3mg/l at site 4 to 7 mg/l at site 15 and probably reflects the increasing proportion of base and inter-flow associated with changing catchment, topography and soil depth.

The percentage differences between the calculated load, derived from winter load-flow data, and the measured loads are shown in Fig. 3. These differences suggest an annual depletion within the river of about 3000 tonnes (as SiO<sub>2</sub>).

Fig 3 suggests that dissolved silicon is removed from the water over longer periods of the year than are normally associated with diatom growth : highest proportional removals were in May 1974 (98%) and August 1976 (95%).

3. Nitrate-N. Concentrations generally displayed the usual seasonal pattern with minimum values in the summer and maximum values in the winter, being 0.13 and 5.0 mg/l respectively at site 15. Using the relationship between residual run-off of catchments and average concentrations in drainage water (Owens *et al*, 1972), and taking account of sewage discharges, there is good agreement with the measured NO<sub>3</sub>-N load from January to April, but during the rest of the year measured flows are lower than those calculated (Fig 4). For the period 1973-6 the calculated load of NO<sub>3</sub>-N upstream of site 15 was equivalent to 12.7 kg/ha.y (with sewage accounting for 12 per cent), the measured discharge being 10.6 kg/ha.y. Inputs in rainfall, 1500 tonnes/y, were 43 per cent of the calculated load to the river.

The apparent loss (2.1 kg/ha.y = 700 tonnes/y) may represent over-estimates in inputs from drainage water (Johnson *et al*, 1969) or subsequent losses within the river from primary production and denitrification (Owens *et al*, 1972).

Using average NO<sub>3</sub>-N yields for different forms of land-use (Owens *et al*, 1972), in the Wye catchment with 22% arable, 51% grassland, 15% rough grazing, 9% forests and 3% urban land, the catchment yield, with sewage, is about 9.6 kg/ha.y.

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#### Table 1

Values of a and b in the equation  $log_{10}C - a + b log_{10}F$  relating the concentrations (C) of calcium and silica to water flow (F) throughout the year at several sites. Non-significant correlations (F>0.05) at certain sites are not included.

Determinand	Site	а	b	r
Calcium	1	0.351	-0.128	-0.516
	4	0.618	0.094	-0.552
	11	1.431	-0.236	-0.585
	13	1.875	-0.329	-0.509
Silica (SiO <sub>2</sub> )	1	0.390	-0.114	-0.917
	4	0.378	0.079	0.322
	10	-0.042	0.340	0.597
	11	-0.238	0.421	0.394
	15	-0.312	0.468	0.429
(Winter months only)	15	1.401	-0.345	-0.924

## Figures

- Fig. 1 The Wye catchment showing geology, major rivers and sampling sites.
- Fig. 2 Means and ranges of calcium concentrations in the main river and the distribution of selected macro-invertebrates.
- Fig. 3 Differences between calculated and measured silcon loads at a downstream site (15) for the period 1973-6 expressed as percentage of calculated load.
- Fig. 4 Calculated and measured monthly loads of  $NO_3$ -N for the period 1973-6 at a downstream site (15).

# Figure 1



# Figure 2



Figure 3



Year

# Figure 4





