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UWIST Paper 1

Water Quality – R. Wye

Introduction

The R. Wye, which is 250 km long and drains an area of 4183 km², rises at Plynlimon (677m O.D.) in Powys, mid-Wales. The Wye catchment is most simply divided into two characteristic geological areas. In the upper catchment (above Erwood, see Table 2) the R. Wye drains generally impermeable Ordivician and Silurian sediments (41% of total catchment), principally mudstones and shales. Below Erwood the river drains mainly the Devonian Old Red Sandstone series (55% of the total catchment) (Fig. 1). A more detailed description of the geology of the Wye catchment is contained in 'Survey of Water Resources and Demands' (Wye River Authority, 1972).

With the proposal to enlarge the Craig Goch Reservoir and regulate the discharge of the R. Wye a general programme of surveillance, designed to provide baseline data for water quality, fisheries (UWIST 1976b) and general ecology (UWIST 1976 d, f) of the R. Wye has been established by UWIST under contract to the Welsh National Water Development Authority.

Water quality data collected routinely by organisations other than UWIST are generally restricted temporally or spatially or with respect to the parameters monitored. Truesdale (1974) analysed samples (Table 1) collected fortnightly from October 1973 to September 1974 from three sites in the upper Wye catchment – R. Wye, at the proposed regulating point, R. Ithon and R. Elan (see Fig. 2). Wye River Division (WNWDA) undertakes routine analyses (Table 1) on water samples collected quarterly from 26 sites in the Wye Catchment: 7 of these sites in the lower catchment are sampled eight times a year. Water abstracted from the R. Wye at Monmouth (ST 512128, 220 km) by Gwent Water Division (WNWDA) is routinely analysed (albuminoid-N, total phosphorus, zinc, lead, copper, cadmium, sodium, potassium, calcium, magnesium) are analysed less frequently. Data provided from these services and the UWIST water quality programme should provide a basis for evaluating the effects of the proposed Craig Goch scheme on the water quality of the R. Wye.

This report is in three parts: the first deals with the main routine water quality programme (i. Routine Water Quality), the second with a localised study of dissolved oxygen concentrations in the lower Wye associated with plant growth during the summer (2. Dissolved Oxygen) and the third with special observations undertaken at the time of supplementary and experimental releases of water (freshets) from Caban Coch Reservoir, in the Elan Valley (3. Freshet Releases from Caban Coch). The three parts are treated separately.

1. <u>Routine Water Quality</u> <u>Methods and Sampling Sites</u>

Water samples have been collected from fourteen sites on the R. Wye and tributaries, generally at fortnightly intervals since April 1975 (Table 2, Figs 1 and

2). Sampling and analytical methods and the frequency of analyses have been described elsewhere (UWIST 1975a) and b). These conditions still apply with the exception of analyses for particulate carbon, humic acid, pesticides and total phosphorus which have not been undertaken on a routine basis. It is important to note that at each sampling occasion samples are not contemporary, neither are samples related to the travel time of water between sites. Thus, site 4 was generally sampled at 10.00 h, site 8 at 12.00 h and site 13 at 16.00 h.

In August, after a prolonged period of dry weather, samples were collected from a number of sites in the headwaters of the R. Wye (Table 3), in an area where there are disused mine workings, and analysed for soluble metals.

Mean daily discharges, estimated from continuous records from gauging stations (Table 2, fig. 2) are generally only available until June 1975. Where such data are not available, records of stage-height have been used to estimate discharge using established stage-discharge relationships: such estimates may be in error by \pm 15% (Wye River division, pers. comm.).

<u>Results</u>

A summary of the results obtained from analyses performed between 7th April and 20th November 1975, is presented in Appendix 1.

Water Quality: spatial aspects

Consideration of the changes of average concentrations of quality parameters along the length of the R. Wye indicate three patterns (Fig 3). With most substances the average concentration increases with increasing distance from the source, particularly below site 11 (e.g. dissolved solids, calcium, suspended solids). The average concentrations of some substances (e.g. silica, free CO₂, copper, nickel) were generally similar along the length of the river.

The third pattern of change, exemplified by concentrations of zinc and nickel was of decreasing concentration downstream, particularly in the upper 60 km of the river. Results from samples collected from the headwaters of the R. Wye in August indicated concentrations of soluble metal considerably higher than total metal concentrations recorded from routine sampling sites (Table 3). The main sources of metal contamination were clearly H1, the Nant Iago, which received drainage from lead mine workings and H4, a small stream draining disused quarry workings.

Of the tributaries, the R. Irfon was of generally similar quality to the R. Wye, while the impounded R. Elan generally contained lower concentrations of most substances than the R. Wye in the upper reaches. The diluting effect of the R. Elan was particularly obvious at site 6 when the compensation flow of the R. Elan contributed a large proportion (up to 84%) of the water below the confluence with the R. Wye. The rivers Ithon and Lugg always carried higher concentrations of dissolved material than the R. Wye at their respective confluences. Indeed, the R. Lugg substantially increased concentrations of many substances recorded at site 13 on the R. Wye (Fig 3.).

Water Quality: Temporal aspects

Only in a few instances could seasonal changes in water quality, not related to flow, be detected. There was little seasonal change in concentration of NO_3 -N in the upper catchment of the r. Wye (site 4, fig. 4) but in the lower catchment, where concentrations were much greater, highest concentrations were recorded during the period April to July: this increase is possibly related to the use and leaching of nitrogenous fertilizers.

Chlorophyll <u>a</u> concentrations in the upper reaches of the R. Wye were generally low (< $5mg/m^3$) during the period when analyses were undertaken (Fig. 4). However, at sites in the middle and lower reaches and on the R. Ithon and R. Lugg chlorophyll <u>a</u> concentrations were elevated during the period May to September (Fig. 4). Peak concentrations at different sites were not synchronous. Maximum concentration of chlorophyll <u>a</u> in the R. Wye was 71 mg/m³ at site 12 during June and the maximum recorded in the catchment was 98 mg/m³ at site 14 (R. Lugg) during August.

Concentrations of silica at sites throughout the catchment displayed no general discernible pattern (Fig 4).

Concentration-flow relationships

The relationship between the concentration $^{\odot}$ of each quality parameter and the flow (F) was tested at each site where flow data were available using:-

Log C = a log F + b

Regression lines were fitted using the method of least squares. Correlation coefficients were calculated and tested for significance using student's 't'. The correlation coefficient ® and regression coefficients are shown in Table 4.

The regression lines, for significant correlations, of flow against calcium and silica concentrations are shown in Fig. 5. Generally most quality parameters at most sites show decreasing concentrations with increasing flow and this is illustrated for calcium in Fig. 5.

Except for site 1, silica concentrations increase with increasing flow and comparison of the slopes of the regression at sites 4, 10 and 11 indicate that the rate of increase in concentration per unit flow increases at downstream sites.

It is possible to interpret the silica data as evidence of a run-off with a constant silica content being utilized in relation to retention time within the river – hence the decrease in concentration downstream at low flows i.e. long retention times. The data certainly suggest that at high flows the silica concentration in the river water is constant throughout the catchment.

Catchment Budgets

Using flow-frequency curves and load-flow regression equations for site 10 (Erwood) and site 13 (Redbrook), tentative catchment budgets have been calculated for dissolved solids, suspended solids, No₃-N and calcium (Table 5). Although the lower catchment (below site 10, Erwood) has considerably greater annual loads per unit of catchment area of calcium, No₃-N and suspended solids, the dissolved loads are similar (Table 5).

Discussion

In general results from this study confirm those water quality data already available for the Wye catchment from other sources (Truesdale 1974; Wye River Division, pers. comm.; Gwent Water Division, pers. comm.). the increased enrichment of the R. Wye downstream, particularly below site 11, is probably related to the geology and land-use in the Wye catchment. Above site 10 the Wye drains impermeable shales and mudstones: below site 10 it drains principally permeable Old Red Sandstone and the more fertile river valley is subject to more intensive agriculture. Such use is reflected in the substantially greater load of NO₃-N in the lower catchment, probably derived from nitrogenous fertilizers, compared with the upper and middle catchment. The annual loss of NO₃-N from the R. Wye (0.38 tonnes/km²) is less than that recorded for the R. Frome (1.14 tonnes/km²), R. Yare (1.4 tonnes/km²) and R. Tud (1.0 tonne/km²) (Casey 1965, Edwards 1973).

Consideration of concentrations of chlorophyll <u>a</u> in the lower reaches in the R. Wye indicated that substantial growths of 'planktonic' algae occurred during summer periods. Peaks of algal density were not synchronous at different sites as was reported by Lack (1971) for the R. Thames. Oscillations in the concentration of silica at sites in the lower reaches during summer months probably resulted from the utilisation of silica by diatoms: Furet (pers. comm.). recorded peaks of, principally centric, diatoms at site 13 in late July and early September and this coincided with reductions in silica concentration.

Many of the relationships between concentrations of quality parameters and flow in the Wye catchment do not confirm relationships established by Edwards (1973 [a]) for East Anglian rivers who found that the concentration of most substances was independent of flow. From Table 4 it will be seen that, in the R. Wye, concentrations generally decline with increasing water flow.

2. Dissolved Oxygen

Methods

Dissolved oxygen and temperature were monitored continuously during June, July and August at Ross-on-Wye (site A, ST 588242), Goodrich (site B, ST 582193) and Symonds Yat (site C, ST 564182) (Fig. 2) using submersible water quality monitors (Briggs and Melbourne 1968). Several faults developed in the monitors which limited the period when reliable records were available. Spot checks indicated that records presented in this report were within the error limits designated by the manufacturers: temperature $\pm 0.5^{\circ}$ c, dissolved oxygen concentration $\pm 6\%$ saturation.

Results

Marked diel changes in oxygen concentration were recorded at all three monitoring sites (A, B and C, Fig. 2) in the lower reaches of the R. Wye during, June, July and August (Fig. 6). The maximum amplitudes of these changes were similar at all sites and were recorded during June (Table 6, Fig. 6) when macrophytes, principally *Ranunculus fluitans*, were growing vigorously (UWIST 1976, 6).

Changes in oxygen concentrations reflected changes in the daily sum of sunlight hours recorded at a nearby meteorological station (Fig. 6.) The periods immediately preceding (7-14 July) and following (14-21 July) the disappearance of the macrophytes (UWIST 1976, 6) were characterized by similar oxygen regimes (Table 6).

Maximum dissolved oxygen concentrations were recorded between 13.00 and 17.45, minima between 05.00 and 06.00.

Discussion

Diel changes in dissolved oxygen concentrations in shallow water bodies with substantial growths of macrophytic plants have been described in detail by many workers (Odum 1956; Edwards and Owens 1965): such changes result from the photosynthetic and respiratory activities of aquatic plants. Diel rhythms in dissolved oxygen in the R. Wye can be principally attributed to the growths of *Ranunculus* in the lower reaches (UWIST 1976, f). Subsequent to the loss of these plants in mid-July, continued diel changes in concentration probably resulted from the growth of both benthic and 'planktonic' algae. Clearly where such oscillations occur, routine sampling techniques are unlikely to record those periods when oxygen concentrations are lowest i.e. dawn. Although substantial amounts of plant material were available for decay at death in mid-July (UWIST 1976, F) no massive de-oxygenation was recorded at the monitoring sites suggesting that much of the material was carried downstream and probably deposited in the estuary.

It is known that the 'long-sustainable' swimming speeds of salmonid species decline with any considerable reduction in the concentration of dissolved oxygen below air-saturation (Doudoroff and Shumway 1970). For example, the swimming speed of coho salmon was reduced by 10% at 5mg $O_2/1$, by 30% at 3mg $O_2/1$ and by about 40% at 2.5mg $O_2/1$. since, in clear waters, salmon are likely to move at dusk, dawn or night rather than during the day (Banks 1969, Hayes 1953) the effects on migrating salmon of low oxygen concentrations during periods of darkness, resulting principally from the respiratory activity of submerged plants, may be significant. Krogius (1954), cited in Banks (1969), showed that salmonid movement was indirectly related to light intensity through the effect of ligh on photosynthesis (presumably affecting oxygen concentrations) and temperature.

3. <u>Freshet Releases from Caban Coch</u>

Methods

On three occasions during 1975 experimental releases of water (freshets) were discharged from Caban Coch to the R. Elan and subsequently into the R. Wye (Table 7, Fig 7). In conjunction with Wye River Division, UWIST undertook some water quality studies during releases (Table 7). Three sites were generally sampled during each release: R. Elan (4.5 km below Caban Coch), R. Wye above the confluence with the R. Elan and R. Wye below the confluence with the R. Elan (8.0 km below Caban Coch). Hydrological and water quality results have been presented elsewhere (Wye Regulation Group, 1975) and these collected data are not presented in full in this paper.

Results

Artificial freshets were always a small proportion of maximum overspill recorded during 1975 (Fig 7). At gauging stations on the R. Elan and R. Wye the increase in stage resulting from discharged water never exceeded 22 cm (Table 8). The speed of the increased flow in June and July was 2.75 and 2.35 km/h respectively (Table 8).

The increased discharge in the R. Elan in May-June and July, when the temperature of water from Caban Coch was significantly lower than the temperature of the R. Wye, was manifested in lower temperatures in the R. Wye 3m below the confluence with the R. Elan. Knowing the mean temperature (calculated from continuous records) and the discharge of the R. Elan and R. Wye it was possible to calculate the mean temperature below the Elan-Wye confluence (Table 9) assuming no significant heat losses or gains from the water.

Freshets had no substantial effects on dissolved oxygen concentrations which were generally around 100% saturation with respect to air. During all releases visual assessment indicated that the R. Elan and the R. Wye, below the confluence with the R. Elan, carried substantial amounts of suspended material during the period of the release. Maximum concentrations of suspended solids, however, were only 12mg/1 (May-June), 23mg/1 (July), and 11mg/1 (September). Chlorophyll <u>a</u> concentrations in the R. Elan during the May-June freshet increased from about 1mg/m³ to a maximum of 33mg/m³, 6 hours after the release began. After 12 hours the concentration had decreased to 4mg/m³ (Fig. 8). Chlorophyll <u>a</u> concentration in the water issuing from Caban valves was less than 1mg/m³ at this time, indicating that the algal material, chiefly *Microspora, Tambellaria, Navicula* and *Diatoma*, probably originated from the R. Elan. Similar results were observed during July and September freshets with the peaks of chlorophyll concentrations in the R. Elan (17 and 10mg/m³ respectively) being recorded during the first 6 hours of release.

Total manganese and iron concentrations at all stations during the July freshets were directly related to suspended solids concentrations:-

(Fe)	=	0.075 (s.s.)	- 0.025	(mg/l)
(Mn)	=	0.05 (s.s.)	- 0.15	(mg/l)

Thus total iron and manganese concentrations in the R. Elan increased during the freshet release: iron varied between 1.120mg/l (3 hours after the release began) and 0.205mg/l, and manganese between 0.840mg/l (3 hours after the release began) and 0.038mg/l.

Discussion

The 'quantum' discharge of water, as carried out in freshet releases, is not likely to simulate regulation discharges. However, discharges of this sort can be instructive. Total releases from Caban Coch (compensation plus extra freshet water) during May-June and July exceeded the maximum anticipated yield to the R. Wye from the proposed enlarged Craig Goch reservoir in the year 2000 (Featherstone, pers. comm.). Clearly with increases in discharge in the R. Wye below the Elan confluence from 2.23 to 3.02 cumec, maximum increase in stage in the R. Wye is generally likely to be less than 25 cm. Nevertheless, at these low natural flows the release of impounded waters to the R. Wye is likely to have substantial effects on the temperature regime downstream of the point of regulation discharges.

The use of artificial discharges to slough biological growths (algae, bacterial floccs) from the bed of the R. Elan would appear to have considerable potential. The results available suggest that discharges over a period of 6 to 9 hours would have a substantial cleansing effect on the river bed: it would seem that discharges of greater duration would not be any more effective from this viewpoint.

Concentrations of suspended solids recorded during these experiments would not generally be regarded as unacceptably high. However, the origin of much of the suspended material would appear to be biological, having a considerably higher wet : dry weight ratio and lower density than mineral material. The fate of such material is not known but it is likely to be carried further downstream than mineral material and, on settling, it will exert a considerable oxygen demand within sediments.

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Table 1.

Parameter	Balfor*	Wye River Division	Gwent Water Division
Hardness	+	+	+
Alkalinity	+	-	+
Sodium	-	-	+
Potassium	-	-	+
Calcium	-	-	+
Magnesium	-	-	+
Sulphate	-	-	+
Chloride	+	+	+
Colour	+	-	+
Turbidity	+	-	+
Ammoniacal-N	-	+	+
Nitrate-N	+	+	+
Nitrate-N	-	+	-
Albuminoid-N	-	+	+
Soluble phosphorus	-	-	+
Total phosphorus	+	+	+
Silicate	+	-	+
Conductivity	-	+	+
Total suspended solids	-	+	+
Iron	+	-	+
Manganese	+	-	+
Zinc	+	-	+
Lead	+	-	+
Copper	+	-	+
Cadmium	+	-	+
Chromium	+	-	-
Permanganate Value	+	+	+
Biological Oxygen Demand	-	+	-
PH	+	+	+
Dissolved Oxygen	-	+	-
Temperature	-	+	+
Chlorophyll <u>a</u>	-	-	+

Water quality parameters routinely monitored by organisations other than UWIST.

+ = data available

- = no data available

* October 1973 – November 1974 only.

Site	River	Location	NGR	Distance from source (km)	Catchment area (km²)	Av flow (m ³ /sec)
1	Wye	Pant Mawr	SN 843827	7	27.2	1.7
2	Wye	D/S Llangurig	SN 921739	20	-	-
3	Wye	D/S Monmouth	SN 961695	34	-	-
4	Wye	Ddol Farm	SN 975676	37	174	7.0
5	Elan	Dolafallon	SN 955668	-	-	1.5
6	Wye	Newbridge	SO 019582	48	-	-
7	Ithon	Disserth	SO 024578	-	358	7.5
8	Irfon	Cilmery	SN 995507	-	244	9.9
9	Wye	Builth Wells	SO 043512	60	-	-
10	Wye	Erwood	SO 076445	68	1280	38.2
11	Wye	Bredwardine	SO 336447	115	-	47.8
12	Wye	Goodrich	SO 581192	195	-	-
13	Wye	Redbrook	SO 528110	222	4010	71.6
14	Lugg	Mordiford	SO 569375	-	1030	12.1

Routine sampling sites in the Wye catchment

Table 3

Soluble metal concentrations at headwater sites (mg/l)

Site	NGR	Mn	Cr	Fe	Cu	Zn	Cd	Pb
H1	SN 827862	0.012	0.07	0.06	0.012	0.91	0.0039	0.032
H2	SN 829853	0.029	0.13	0.15	0.012	0.49	0.0034	0.027
H3	SN 824853	0.033	0.71	0.17	0.006	0.02	0.0019	0.007
H4	SN 827852	0.047	1.04	0.22	0.006	1.68	0.0043	1.84
H5	SN 825843	0.046	0.24	0.34	0.004	0.02	0.0002	0.008
H6	SN 825843	0.029	0.66	0.15	0.004	0.26	0.0017	0.017
H7	SN 831837	0.026	0.42	0.19	0.005	0.14	0.0005	0.012
H8	SN 864841	0.025	0.36	0.11	0.003	0.12	0.0006	0.006

Regression and Correlation C	oefficients for Concentra	ation-Flow Relationships

Site		1			4			7			8	
Parameter	а	b	r	а	b	r	а	b	r	а	b	r
SiO ₂	-0.09	0.38	-0.82*	0.20	0.34	0.68*	0.36	0.19	0.46	0.34	0.28	0.89*
TDS	-0.03	1.56	-0.13	-0.04	1.70	-0.20	-0.13	2.12	-0.79*	-0.05	1.84	-0.34
Ca ²⁺	-0.14	0.34	-0.65*	-0.09	0.64	-0.56*	-0.20	1.35	-0.93*	-0.16	0.99	0.79*
Mg ²⁺	-0.10	0.01	-0.60*	-0.03	0.18	-0.29	-0.13	0.74	-0.79*	-0.14	0.41	-0.89*
NO ₃ -N	-0.20	-0.73	-0.42	-0.003	-0.36	0.01	-0.04	0.03	-0.13	0.01	-0.32	0.05
HCO ₃	-0.39	0.09	-0.90*	-0.29	0.61	-0.61*	-0.19	1.57	-0.81*	-0.28	1.17	-0.83*
Table 4		10			11			13			14	
(cont.)												
SiO ₂	0.53	-0.23	0.81*	0.63	-0.53	0.62*	-0.20	0.58	-0.18	0.31	0.61	0.44
TDS	0.08	1.80	0.30	-0.17	2.20	-0.62*	-0.26	2.62	-0.65*	0.03	2.48	0.23
Ca ²⁺	-0.10	1.13	-0.41	-0.25	1.50	-0.50	-0.34	2.05	-0.59*	0.13	1.78	0.50
Mg ²⁺	-0.01	0.42	-0.06	-0.12	0.63	-0.45	-0.34	1.25	-0.72*	0.03	0.93	0.18
NO ₃ -N	0.14	-0.38	0.30	0.26	-0.40	0.56*	-0.12	0.46	-0.21	0.26	0.48	0.67*
HCO ₃	-0.04	1.22	-0.08	-0.16	1.65	-0.20	-0.27	2.18	-0.43	0.12	2.00	0.32

Table 5 - Catchment Loads

		Annual Load (Tonnes/year)		Annual lo (Annual load per unit catchment area (Tonnes/year/km ²)			
	Upper/Middle	Lower	Total	Upper/Middle	Lower	Total		
	Catchment	Catchment	Catchment	Catchment	Catchment	Catchment		
Dissolved Solids	3.27 x 10 ⁴	7.33 x 10 ⁴	10.60 x 10 ⁴	25.6	26.9	26.4		
Suspended Solids	0.13 x 10 ⁴	0.91 x 10 ⁴	1.04 x 10 ⁴	0.98	3.42	2.59		
NO ₃ -N	0.029 x 10 ⁴	0.104 x 10 ⁴	0.133 x 10 ⁴	0.22	0.38	0.33		
Ca ²⁺	0.39 x 10 ⁴	1.59 x 10 ⁴	1.98 x 10 ⁴	3.05	5.83	4.94		

Sites	June & July		7-14	July	14-21 July		
	Max.	Min.	Max.	Min.	Max.	Min.	
А	19.1	8.5	12.8	8.7	11.9	6.9	
B*	15.6	5.9	-	-	-	-	
С	15.8	5.0	11.1	5.7	9.8	5.8	

Maximum and minimum concentrations (mg/l) of dissolved oxygen (1975).

* June only.

Table 7

Freshet releases from Caban Coch (1975)

Date	Compensation discharge (cumec)	Extra discharge (cumec)*	Discharge of R. Wye (cumec)	Water Quality Studies
31 May & 1 June	1.53	3.02	0.70	Chl. <u>a</u> , ss. D.O., T.
8 & 9 July	1.53	3.02	0.20	Chl. <u>a</u> , ss, D.O., T. pH, C.Fe. Mn.
9 & 10 September	1.53	1.51	4.00	Chl. <u>a</u> , pH. C.

* over 48 h.

Chl. <u>a</u> = chlorophyll <u>a</u> concentration, ss = suspended solids concentration \neq , D.O. = dissolved oxygen concentration, T = temperature, C = conductivity \neq , Fe = total iron concentration \neq , Mn = total manganese concentration \neq , pH \neq .

 \neq = Wye River Division (W.N.W.D.A.) data.

Stage increases and times of travel of freshets, 31 May – June and 8-10 July

Site	Distance from Caban Coch	Rise (cm)		Time of travel (h)	
	(km)	June	July	June	July
R. Elan (Aberceithon	4	14.0	11.5	0.50	0.50
R. Wye (Llanwrthwl)	8	20.0	20.0	3.00	3.00
R. Wye (Newbridge)	16	10.0	9.0	5.50	6.15
R. Wye (Erwood)	38	18.0	22.0	12.50	12.50
R. Wye (Bredwardine)	83	7.5	11.5	31.50	36.00
R. Wye (Hereford)	106	7.5	12.7	38.50	45.00

Table 9

Mean water temperature (°C) May – June 1975

Period	R. Elan	R. Wye above confluence with R. Elan	R. Wye below confluence with R. Elan	Calculated R. Wye below confluence with R. Elan
12.00 30 May –	8.9	11.2	9.6	9.6
12.00 31 May				
12.00 31 May –	9.3	12.3	10.0	9.7
12.00 1 June				
12.00 1 June –	9.3	11.5	9.9	9.5
12.00 2 June				

Station	1	2	3	4	5*	6	7*
Flow m ₃ s ⁻¹	0.75			2.4	1.4		2.1
	(1.23-0.07)			(9.0 – 0.18)	(1.6 – 1.0)		(8.8 – 0.31)
Temperature °C	11.0	11.7	12.0	11.9	9.7	11.9	13.1
	(17.8-4.9)	(18.4 – 4.9)	(19.1 – 4.9)	(20.0 – 4.9)	(12.4 – 5.0)	(19.3 – 5.0)	(20.5 – 4.8)
Conductivity uS.cm ⁻¹	47	53	59	67	37	53	180
	(64-35)	(66 – 42)	(71 – 45)	(88-54)	(43 – 31)	(71 – 43)	(228 – 126)
рН	6.83	6.43	7.00	7.10	6.17	6.81	7.92
	(7.23 – 6.33)	(7.42 – 6.35)	(7.57 – 6.59)	(7.57)	(6.47 – 5.75)	(7.43 – 6.36)	(9.09 – 7.20)
Alkalinity (Total) mg/1	2.9	4.5	6.5	7.1	0.9	4.4	60.3
CaCO ₃	(5.2 – 0.6)	(8.4 – 1.6)	(11.5 – 2.0)	(12.5 – 2.2)	(3.0 – 0.3)	(7.0 – 1.7)	(87.4 – 31.6)
Free CO ₂ mg/I	1.0	1.5	1.8	1.5	1.6	2.0	2.1
	(1.7 –0.4)	(3.2 – 0.7)	(4.5 – 0.7)	(4.3 – 0.6)	(5.3 – 0.4)	(5.9 – 0.6)	(5.5 – 0.1)
Dissolved solids mg/l	38	41	48	50	29	42	130
	(58 – 17)	(53 – 30)	(68 – 32)	(74 – 27)	(56 – 6)	(61 – 16)	(164 – 99)
Turbidity F.T.U.	1.1	1.1	1.4	1.3	2.2	1.7	6.4
	(2.9 – 0.2)	(2.5 – 0.1)	(3.2 – 0.3)	(3.3 – 0.3)	(5.0 – 1.2)	(3.6 – 0.6)	(22.0 – 1.6)
Colour Hazen	5	5	5	5	15	10	15
	(10 – 0)	(10 – 0)	(15 – 0)	(15 - 0)	(20 – 0)	(15 – 0)	25 – 10)
Chloride mg/l	9.3			10.9			12.7
	(10.1 – 6.6)			(12.7 – 10.1)			(15.7 – 10.9)
Ammonia ⁺ Ug/L-N	11	8	7	6	6	8	5
	(23 – ND)	(18 – ND)	(12 – ND)	(15 – ND)	(9 - 1)	(16 – 1)	(? – ND)
Nitrate ⁺ Ug/L-N	2	1	1	1	2	2	16
	(5 – ND)	(4 – ND)	(3 – ND)	(3 - ND)	(3 – 1)	(5 – ND)	(52 – 2)
Nitrate mg/I –N	0.24	0.38	0.37	0.47	0.27	0.42	1.12
	(0.60 – ND)	(0.70 – 0.20)	(0.70 0 0.20)	(1.00 – 0.26)	(0.60 – 0.10)	(0.70 – 0.20)	(1.70 – 0.67)
Orthophosphate Ug/I –P	18	16	11	18	19	22	73
	(103 – 2)	(75 – ND)	(43 – ND)	(69 – ND)	(80 – ND)	(100 – 1)	(158 – 8)
Silica (reactive mg/l –Sio ₂	2.6	2.5	2.4	2.4	1.7	2.0	2.2
	(3.0 – 2.2)	(3.0 – 1.5)	(3.3 – 0.9)	(3.3 – 1.0)	(2.0 – 1.5)	(2.9 – 1.2)	(5.4 – 0.4)

Appendix 1_ - Average values and ranges of parameters for the period 7/4/75 to 17/11/75

Appendix 1 (contd.) – Stations 1-7

Station	1	2	3	4	5*	6	7*
Sulphate mg/l	6.1			8.0			16.7
	(6.7 – 6.0)			(8.5 – 7.3)			(17.4 – 16.3)
Soluble Organic Carbon	1.6	1.5	1.7	1.7	2.1	1.9	3.4
mg/l	(3.1 – 1.0)	(2.4 – 0.9)	(2.2 – 1.1)	(2.2 – 1.1)	(2.2 – 1.8)	(2.2 – 1.1)	(4.9 – 1.5)
Suspended Solids mg/l	0.7	1.1	0.9	1.1	1.4	1.5	6.8
	(2.4 – 0.1)	(5.2 – 0.2)	(3.2 – 0.2)	(3.0 – 0.2)	(6.0 - 0.8)	(4.8 – 0.7)	(33.6 – 1.5)
Ash mg/l	0.2	0.3	0.3	0.4	0.7	0.7	4.2
	(0.8 – ND)	(2.8 – ND)	(2.3 – ND)	(1.8 – ND)	(5.0 – ND)	(3.7 – ND)	(29.5 – 0.5)
Sodium mg/l	5.7			6.7			8.7
	(6.1 – 4.2)			(8.8 – 5.7)			(10.4 – 7.7)
Potassium mg/l	0.59			0.87			2.15
	(0.64 – 0.40)			(1.15 – 0.75)			(3.61 – 1.46)
Calcium mg/l	2.5	3.3	4.1	4.3	1.7	3.4	22.4
	(3.4 – 1.1)	(4.7 – 2.4)	(5.4 – 2.9)	(6.1 – 3.2)	(2.0 – 1.2)	(4.4 – 1.9)	(30.9 – 15.7)
Magnesium mg/l	1.1	1.3	1.5	1.5	0.8	1.3	5.4
	(1.6 – 0.9)	(1.5 – 1.1)	(1.7 – 1.2)	(1.8 – 1.3)	(1.0 – 0.6)	(1.7 – 1.0)	(6.5 – 3.6)
Total hardness mg/l CaCO ₃	10.8	13.6	16.4	16.9	7.5	13.8	78.1
	(15.1 – 6.3)	(17.9 – 10.5)	(20.5 – 12.2)	(22.7 – 13.3)	(9.1 – 5.5)	(18.0 – 8.9)	(103.9 – 54.0)
Cadmium µg/l	3	3	1	2	1	1	1
	(4 – 2)	(4 – 2)	(1 – ND)	(6 – ND)	(2 – ND)	(2 – ND)	(3 – ND)
Copper µg/I	5	5	4	2	2	5	4
	(7 – 4)	(6 – 4)	(6 – 1)	(5 – ND)	(5 – 1)	(6 – 3)	(5 – 4)
Iron µg/l	60	50	60	60	250	170	210
	(90 – 30)	(60 – 40)	(80 – 40)	(60 – 50)	(340 – 160)	(190 – 160)	(270 – 110)
Manganese µg/l	32	14	12	10	85	21	30
	(38 – 24)	(21 – 10)	(22 – 6)	(19 – 1)	(100 – 77)	(31 – 14)	(42 – 20)
Nickel µg/l	50	60	50	50	60	40	90
	(150 – ND)	(190 – ND)	(110 – ND)	(150 – ND)	(110 – ND)	(110 – ND)	(150 – ND)
Lead µg/I	3 (9 – ND)	ND	ND	ND	ND	ND	ND
Zinc µg/I	154	54	41	29	23	26	9
	(190 – 110)	(56 – 50)	(63 – 25)	(47 – 13)	(30 – 18)	(40 – 15)	(19.4)

* Tributaries

ND = Not detactable.

Appendix 1 (contd.) – Stations 8-14

Station	8	9	10	11	12	13	14
Flow m ₃ s ⁻¹	0.75		11.7	15.8		27.4	4.23
	(10.2 – 0.24)		(46.0 – 2.9)	(59.0 – 5.0)		(72.0 – 7.8)	(9.8 – 1.8)
Temperature °C	12.9	13.3	12.8	13.6	14.3	14.6	13.3
	(21.5 – 5.0)	(21.5 – 5.0)	(22.0 – 5.0)	(22.5 – 5.6)	(22.5 – 5.7)	(21.5 – 5.4)	(21.0 – 5.2)
Conductivity uS.cm ⁻¹	90	88	100	149	262	282	410
	(116 – 75)	(97 – 74)	(124 – 81)	(193 – 100)	(379 – 141)	(361 – 156)	(497 – 308)
рН	7.46	7.54	7.65	7.92	8.16	8.27	8.38
	(8.11 – 6.91)	(7.77 – 7.02)	(8.10 – 7.17)	(8.86 – 7.28)	(8.87 – 7.94)	(8.74 – 7.74)	(8.85 – 8.01)
Alkalinity (Total) mg/1	22.3	19.1	24.1	50.7	104	115	185
CaCO ₃	(36.5 – 11.0)	(28.2 – 10.6)	(36.2 – 12.9)	(76.8 – 12.9)	(169 – 34)	(162 – 59)	(206 – 128)
Free CO₂ mg/I	1.4	1.6	1.4	1.6	1.7	1.5	1.9
	(3.8 – 0.6)	(3.8 – 0.6)	(2.6 – 0.6)	(4.5 – 0.2)	(3.7 – 0.3)	(2.9 – 0.4)	(4.2 – 0.5)
Dissolved solids mg/l	68	71	75	104	180	195	293
	(89 – 46)	(96 – 56)	(110 – 44)	(140 – 72)	(259 – 108)	(262 – 117)	(325 – 169)
Turbidity F.T.U.	2.3	4.1	3.8	5.5	7.2	8.0	5.5
	(4.8 – 0.7)	(12.2 – 0.7)	(10.5 – 0.9)	(17.0 – 0.9)	(25.0 – 1.8)	(27.6 – 0.9)	(17.5 – 1.0)
Colour Hazen	10	10	10	10	10	10	5
	(20 – 5)	(20 – 5)	(20 – 5)	(20 – 5)	(15 – 5)	(15 – 5)	(15 – 0)
Chloride mg/l	9.1		11.0	12.0		17.4	19.9
	(11.8 – 8.1)		(13.7 – 8.8)	(12.8 – 11.4)		(23.2 – 13.9)	(24.5 – 16.3)
Ammonia ⁺ Ug/L-N	13	8	14	19	16	23	27
	(25 – 2)	(17 – ND)	(61 – ND)	(93 – ND)	(31 – 3)	(75 – ND)	(70 – 6)
Nitrate ⁺ Ug/L-N	4	4	5	9	24	22	28
	(14 – ND)	(13 – ND)	(12 – ND)	(21 – 2)	(46 – 5)	(37 – 11)	(30 – 11)
Nitrate mg/I –N	0.51	0.52	0.61	0.87	2.11	2.09	3.96
	(0.80 – 0.24	(0.90 – 0.26)	(1.00 – 0.26)	(1.50 – 0.50)	(4.10 – 0.96)	(3.5 – 1.04)	(5.00 – 3.10)
Orthophosphate µg/I –P	29	36	35	24	160	145	205
	(135 – 3)	(122 – 3)	(142 – 7)	(81. – 4)	(327 – 77)	(297 – 60)	(342 – 83)
Silica (reactive mg/I –Sio ₂	2.2	2.1	2.1	1.7	2.1	2.4	5.4
	(3.9 – 1.4)	(3.8 – 1.0)	(4.0 – 0.9	(3.9 – 0.3)	(3.7 – 0.6)	(5.3 – 0.7)	(7.4 – 2.8)

+ Results cover the period 7/4/75 to 14/7/75 only.

Appendix 1 (contd.) – Stations 8-14

Station	8	9	10	11	12	13	14
Sulphate mg/l	9.5		11.5	14.0		23.9	32.0
	(10.7 – 8.9)		(11.8 – 11.2)	(14.5 – 13.5)		(24.8 – 22.7)	(37.9 – 27.0)
Soluble Organic Carbon	1.9	2.3	2.4	2.5	4.0	3.4	2.7
mg/l	(2.8 – 0.8)	(2.8 – 1.6)	(3.1 – 1.3)	(3.3 – 1.4)	(16.6 – 2.2)	(9.5 – 2.1)	(9.8 – 1.7)
Suspended Solids mg/l	2.2	3.6	3.4	6.2	8.8	9.1	4.5
	(5.1 – 0.4)	(9.2 – 1.4)	(13.6 – 0.7)	(26.5 – 1.5)	(61.5 – 1.7)	(60.9 – 1.9)	(21.9 – 1.1)
Ash mg/l	1.1	2.3	2.3	4.0	6.1	6.1	2.3
	(3.5 – ND)	(3.1 – 0.2)	(1.2 – 0.2)	(22.3 – 0.2)	(52.4 – 0.7)	(50.8 – 0.7)	(8.3 – 0.5)
Sodium mg/l	6.0		6.5	7.4		11.5	13.0
	(7.9 – 5.2)		(7.0 – 6.1)	(7.6 – 6.8)		(15.3 – 9.2)	(15.6 – 10.8)
Potassium mg/l	1.25		1.30	1.77		2.99	4.01
	(1.74 – 1.07)		(1.40 – 1.25)	(2.01 – 1.53)		(4.15 – 2.33)	(6.10 – 2.66)
Calcium mg/l	8.5	7.9	10.5	16.0	35.2	41.7	62.0
	(14.7 – 6.5)	(10.1 – 4.9)	(14.7 – 6.5)	(29.0 – 10.2)	(55.2 – 15.6)	(78.8 – 17.6)	(76.5 – 35.0)
Magnesium mg/l	2.4	2.3	2.6	3.2	53	6.5	8.5
	(3.2 – 1.7)	(2.8 – 1.9)	(3.2 – 2.0)	(3.9 – 2.3)	(7.5 – 2.5)	(9.1 – 3.5)	(9.3 – 7.0)
Total hardness mg/l CaCO ₃	31.1	29.2	39.4	53.1	109.7	130.9	189.9
	(49.9 – 23.2)	(36.7 – 20.0)	(49.9 – 24.4)	(88.5 – 34.9)	(168.8 – 49.3)	(234.3 – 58.4)	(229.4 – 116.2)
Cadmium µg/l	2	2	1	1	1	1	2
	(3 – ND)	(3 – ND)	(2 – ND)	(2 – ND)	(2 – ND)	(2 – ND)	(3 – ND)
Copper µg/I	4	4	5	3	7	6	13
	(5 – 3)	(6 – 2)	(6 – 2)	(7 – 2)	(8 – 6)	(7 – 4)	(23 – 8)
Iron μg/l	100	170	110	130	80	130	90
	(120 – 60)	(200 – 130)	(180 – 60)	(210 – 90)	(110 – 50)	(210 – 80)	(130 – 50)
Manganese µg/I	13	21	12	23	16	28	?
	(16 – 8)	(30 – 15)	(17 – 9)	(33 – 13)	(17-15)	(57 – 9)	(26 – 3)
Nickel µg/l	50	60	50	20	180	130	530
	(150 – ND)	(110 – ND)	(90 – ND)	(70 – ND)	(260 – ND)	(160 – ND)	(1290 – ND)
Lead µg/I	ND	3	3	5	2	5	3
		(10 – ND)	(9 – ND)	(15 – ND)	(7 – ND)	(14 – ND)	(10 – ND)
Zinc Ua/I	17	21	10	11	11	15	16
	(37 - 4)	(41 – 10)	(19 – ND)	(21 – ND)	(15 – 7)	(20 – 11)	(37 – 3)

* Tributaries

ND = Not detectabl

Figure 1

Sampling sites, catchment area & geology of R. Wye



Figure 2 Sampling sites in the Wye Catchment



Figure 3 Concentration variations within catchment



Figure 4

Temporal variations of some parameters



Figure 5

Concentration/flow relationships for Calcium & Silica



Figure 6

Fluctuations in dissolved oxygen concentrations and sunshine hours – Goodrich 1975





Figure 7

Figure 8

Changes in the concentration of chloropyll <u>a</u> 30 May – 2 June 1975 Nominal release period from Caban Coch, 09.00 31 May – 09.00 2 June

