Sediment and Stream Water Quality in a Changing Environment: Trends and Explanation
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WATER QUALITY TRENDS IN THE WINDRUSH CATCHMENT: NITROGEN SPECIATION AND SEDIMENT INTERACTIONS

P. J. JOHNES
Department of Environmental & Evolutionary Biology, University of Liverpool, Liverpool L69 3BX, UK
T. P. BURT
School of Geography, University of Oxford, Oxford OX1 3TB, UK

ABSTRACT For the predominantly agricultural River Windrush catchment, spatial variations in concentrations of nitrogen species and suspended sediment were strongly related to geology and land use. Temporal patterns of NO_3^- and NO_2^- concentrations during the three year study were highly correlated with seasonal variations in baseflow. Suspended sediment concentrations were mainly controlled by storm discharge. Variations in total ammonium concentrations reflected both flow controls. Suspended sediment effects total ammonium and organic nitrogen transport to the aquatic system, and in-stream cycling processes. Organic nitrogen did not display consistent seasonal variations, but concentrations occasionally exceeding those of NO_3^-. Overall, NO_3^- and organic nitrogen were the most important at 60% and ~40%, of total nitrogen load, respectively. Future assessments of agriculture impact on river water quality should consider the total nitrogen load, and not solely that of NO_3^-.

INTRODUCTION

Modern agriculture has long been recognized as a significant non-point source of water pollution. Considerable progress has been made in appraising the pollutants produced from this source: sediment, pesticides, chemical fertilizers, and animal wastes. Studies of the impact of changing agricultural practice and land use on water quality typically have focused on trends in sediment and NO_3^- concentrations and loads, and, recently, on sediment quality to provide a wider context for understanding the nature and origins of such impacts (e.g. Ongley, 1982; Walling & Moorehead, 1987). Despite this earlier work, assessments still need to be made of a wider range of agriculturally-derived pollutants, particularly of nitrogen speciation, and sediment in the aquatic environment.

For the study described herein, concentrations and fluxes of various nitrogen species and suspended sediment were investigated in a three year research program (Johnes, 1990). The distributed approach involved sampling at a range of temporal and spatial scales. The study was conducted in the catchment of the River Windrush, a tributary of the Thames. The basin is representative of a wide range of predominantly agricultural rural lowland regions, which have mixed geology and land use, and a relatively low population density. In-stream nitrogen speciation and suspended sediment were quantified with respect to short-term, seasonal and annual trends in concentration and load for two successive water years (WY): October 1987 to September 1988, WY88, was wet; and October 1988 to September 1989, WY89, was dry.

SITE DESCRIPTION

The Windrush rises on the Cotswold escarpment (300-240 m OD), and flows south-eastwards down the Cotswold dip slope to join the Thames at Newbridge (70 m OD), 20 km above Oxford (see Fig. 1). The catchment area above Newbridge is 362.6 km^2. The rocks of the catchment are Jurassic in age and are mainly resistant limestones with the lower Windrush excavated in softer Oxford Clay.

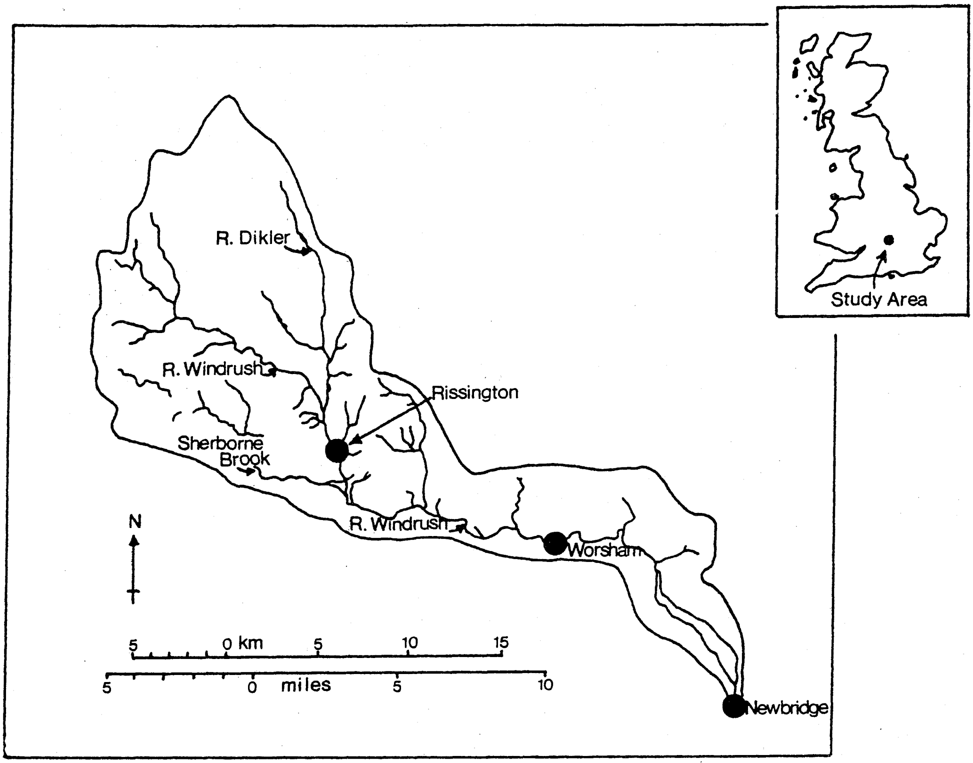

FIG. 1 Map of the Windrush catchment.

The limestone plateau of the upper basin is deeply incised by the River Windrush and its major tributaries, the River Dikler and the Sherborne Brook. On the whole, tributary development throughout the catchment is poor, with dry tributary valleys a classic feature of the upper limestone plateau. The relative proportion of river flow derived from surface, subsurface and groundwater sources varies along the length of the Windrush, because the river flow is affected by intermittent hydraulic contact with the limestone aquifer. In the upper basin, flow is derived primarily from springs issuing from the limestone. In contrast, the middle reaches of the Windrush receive a significant portion of their flow from near-surface runoff as the river meanders over a broad Lias Clay floodplain.

Mean annual rainfall varies across the catchment ranging from 810 mm in the north west plateau area to 680 mm in the south east of the catchment. The flow regime of the Windrush is similar to that reported for other chalk and limestone catchments (Burt, 1991) and is characterized by minimum flows in August and maximum flows in January

The catchment land use was determined from a survey of all land owners in the catchment. In general, the land is used for agriculture with settlements confined to three small towns, isolated villages, and farmsteads. The majority of the river corridors are used for permanent pasture, and intensive dairying is common in these areas. On the slopes and in the limestone plateau regions, the land is used for intensive cereal and oilseed rape cultivation, and fodder cropping for arable sheep enterprises. Permanent pasture, rough grazing and woodland occur where the steepness of the dry valleys precludes cultivation. Livestock farming in the Windrush catchment generally is intensive and based on sheep and cattle rearing.

APPROACH AND METHODS

The general approach of the research program involved three phases of data collection: water quality sampling; discharge measurements for subsequent calculation of nutrient and sediment load; and land use survey to detail the nutrient and sediment export zones within the catchment.

Sampling strategy

The sampling strategy employed involved collection of water samples on two temporal scales (daily, and hourly during periods of increased flow); periodic spatial sampling; and periodic sampling of point source discharge from tile drains and springs.

Spatial sampling Monthly samples were collected from 20 sites on the River Windrush and from each major tributary just upstream of its confluence with the Windrush.

Temporal sampling Two sites provided daily water samples over the study period. One site, at the top of the Lias Clay floodplain at Rissington (Fig. 1), was instrumented with two Rock and Taylor water samplers. One sampler was stage-activated for use during storms. The other sampler took daily samples. An autographic stage recorder (Ott R16) and a stage board also were installed at this site. Discharge was determined periodically using the rated section technique. A log-linear rating relation between stage and discharge was derived from instantaneous discharge and stage observations. Discharge was computed from the rating and continuous stage records. The second site, at the Thames Water Authority gaging station at Worsham in the southeast of the catchment, was sampled daily by hand. At this site, discharge was computed from a rating for the twin adjustable radial (sharp crested) weir and continuous stage.

Periodic sampling of springs and tile drains Point source discharges of nutrients and sediments into the River Windrush were sampled to evaluate their contribution to the nutrient and sediment loading and patterns in the Windrush. This involved hand sampling of tile drains and ditches throughout the WY89. Springs also were sampled weekly throughout this period to give an estimate of groundwater composition.

Sample preservation, storage and analysis

All samples were collected in 500 ml acid washed polyethylene bottles. Prior to collection, 5 ml of 40 mg l^{-1} mercuric chloride was added to each bottle as a biocidal preservative. Samples collected by hand were filled completely to eliminate air and hence inhibit aerobic biological action. Suspended sediment concentrations were determined by vacuum filtration onto 0.22 μm Millipore membrane filters. Subsamples were taken of each water sample before and after filtration to allow subsequent distinction between dissolved and particulate fractions. Samples were stored at 4°C in the dark prior to nutrient analysis.

All samples were analyzed for nitrogen species (nitrate, NO_3^-; nitrite, NO_2^-; total ammonium, NH_3 & NH_4^+; total organic nitrogen, T.ORG-N, including dissolved – D.ORG-N and particulate – P.ORG-N, which was determined by difference) and suspended sediment (SS). Samples also were analyzed for total phosphorus. Inorganic nitrogen species were analyzed using standard autoanalytical colorimetric procedures. Total nitrogen (TN) and phosphorus (TP) were determined simultaneously using a persulfate oxidation digestion modified for a microwave digestion unit. This procedure converted all nitrogen to NO_3^- and all phosphorus to ortho-phosphate (PO_4-P). The digested samples were subsequently analyzed using standard auto-analytical procedures.

RESULTS

Spatial variation in nitrogen species & suspended sediment concentrations

The nitrogen speciation and SS balance vary among the main River Windrush, the River Dikler and the Sherborne Brook. In all three, the maximum NO_3-N concentrations equal and occasionally exceed the EEC limit of 11.3 mg l^{-1}. NO_3-N plus ORG-N constituted between 95 and 99% of the TN load. The Sherborne Brook, which is largely spring-fed and has no outcrops of clay within its boundaries, has significantly higher NO_3^- and ORG-N concentrations (40 sample mean 9.8 mg l^{-1} NO_3-N, 7.1 mg l^{-1} ORG-N) than either the River Windrush (9.2 mg $l^{-1}$$NO_3$-N, 5.9 mg l^{-1} ORG-N), or the River Dikler (8.4 mg l^{-1} NO_3-N, 4.7 mg l^{-1} ORG- N) which receives a lower proportion of its flow from groundwater. The concentrations of NO_2^-, total ammonium, and SS exhibit reverse trends, with the highest concentrations recorded in the River Dikler, and the lowest at the Sherborne Brook. In addition, the SS concentrations in the River Windrush increased markedly as the river flowed on to the Lias Clay floodplain at Rissington, particularly where the whole floodplain area had been recently ploughed and under-drained.

Temporal trends in nitrogen species and suspended sediment concentrations

Daily sampling The WY88 was very wet, giving rise to high water flow in the Windrush and tributary streams, with long periods of overbank flow occurring in the period December 1987 to March 1988 (Fig. 2). The WY89 was conversely very dry, with a mild winter.

Variations in NO_3^- concentrations are highly correlated (r^2=0.41, p<0.001) with discharge for 866 observations at Worsham. Peak NO_3^- concentrations occur in the winter periods, with higher levels observed in the wetter winter. At both Rissington and Worsham,

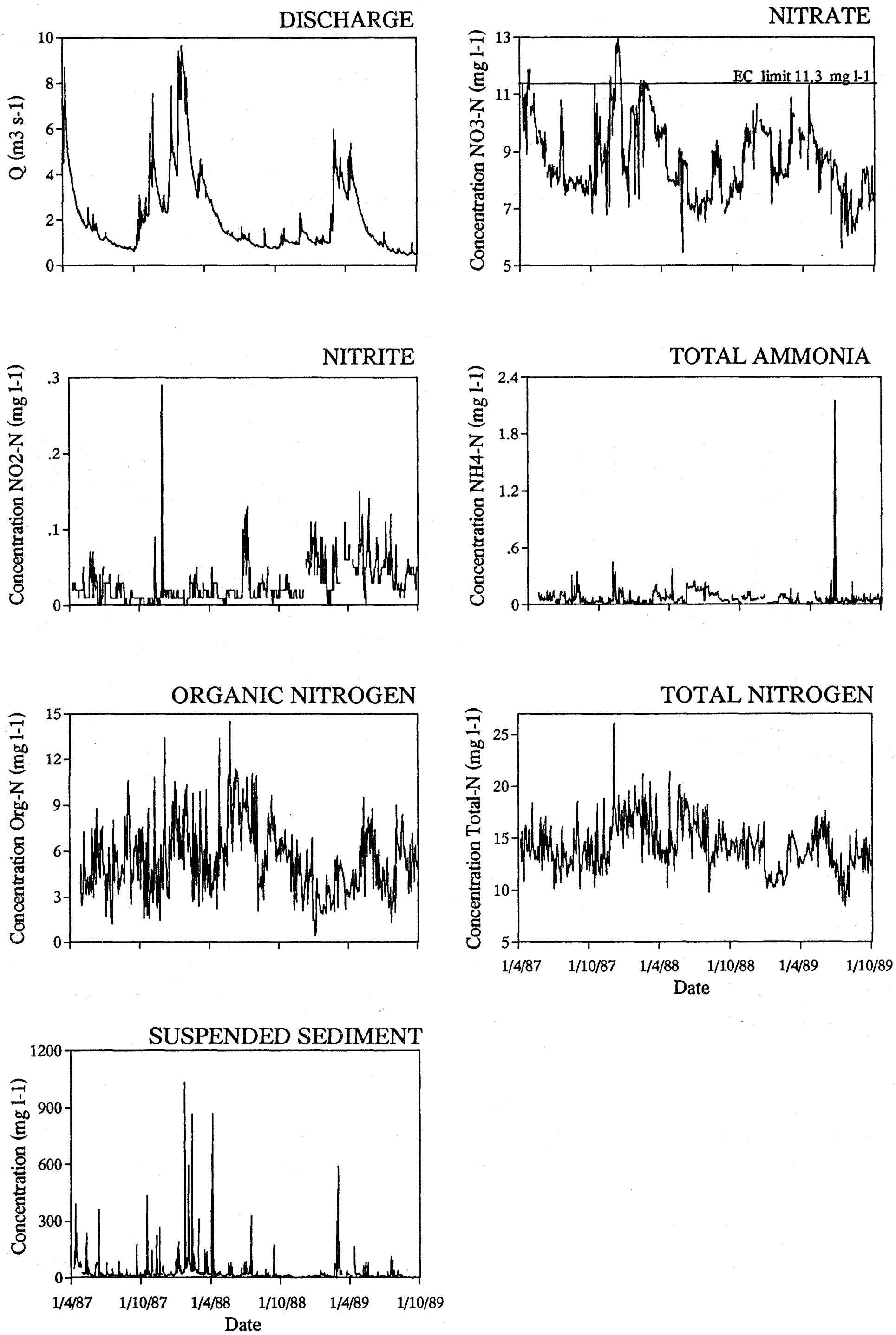

FIG. 2 Variations in discharge, nitrogen species and suspended sediment concentrations at Worsham, 1987-1989.

whilst most NO_3^- concentrations fall below the EEC limit (11.3 mg l^{-1}), winter maxima can exceed this level for short periods. During winter, high NO_3^- concentrations combine with high discharge producing high NO_3^- (cf. Burt *et al.*, 1988).

The NO_2^- concentrations observed were found to be close to the lower limit of detection of the analytical procedure, and thus do not show great variability over time. Nevertheless, broad trends are apparent at both sites. For the most part concentrations fall below 0.1 mg l^{-1} NO_2-N, with early summer maxima apparent in both water years. Concentrations are significantly higher in the drier summer period, increasing earlier in the year. Thus NO_2^- concentrations appear to increase at lower flows, presumably when the dissolved oxygen concentrations in the river are reduced.

TABLE 1 Annual loads carried by the River Windrush at Rissington and Worsham for WY88 and WY89.

	Rissington 1987-1988			Worsham 1987-1988			Rissington 1988-1989			Worsham 1988-1989		
	Tonnes	kg ha-1	%Total	Tonnes	kg ha-1	%Total	Tonnes	kg ha-1	%Total	Tonnes	kg ha-1	%Total
NO3-N	345.61	20.041	60.11	833.44	28.157	59.79	278.10	16.125	58.27	598.29	20.212	58.98
NO2-N	1.43	0.083	0.25	2.60	0.088	0.19	1.73	0.100	0.36	2.18	0.074	0.21
NH4-N	7.06	0.409	1.23	8.07	0.273	0.58	4.54	0.263	0.95	6.01	0.203	0.60
Total IN-N	354.10	20.532	61.59	844.11	28.518	60.54	284.37	16.488	59.58	606.48	20.489	59.79
D.OR-N	100.90	5.851	17.42	310.50	10.490	22.27	80.81	4.686	16.94	223.22	7.541	22.01
P.OR-N	120.71	6.999	20.99	239.97	8.107	17.21	112.07	6.498	23.48	184.67	6.239	18.20
Total OR-N	221.61	12.850	38.41	550.47	18.597	39.48	192.88	11.184	40.42	407.89	13.780	40.21
Total N	575.71	33.382	100.00	1394.58	47.115	100.00	477.25	27.672	100.00	1014.37	34.269	100.00
T.D-P	7.24	0.420	54.68	20.34	0.687	61.76	7.31	0.424	58.71	8.75	0.295	55.73
T.P-P	6.00	0.348	45.32	12.59	0.425	38.24	5.14	0.298	41.29	6.95	0.235	44.27
Total P	13.24	0.768	100.00	32.93	1.112	100.00	12.45	0.722	100.00	15.70	0.530	100.00
Susp-sed	1327.29	76.962		6915.39	233.63		889.61	51.580		2353.62	79.51	

Ammonium concentrations in the Windrush cover a wide range with the majority falling below the EEC limit of 0.25 mg l^{-1} NH_4-N. However, peak concentrations reached 2 mg l^{-1} at Worsham and 6 mg l^{-1} at Rissington during periods of higher flow, and in association with peak SS concentrations. Ammonium exhibits bi-annual maxima. In wetter years, the maxima peak in winter corresponding with periods of high flow and SS transport, with a secondary base concentration peak in the mid-summer period. In drier years, maxima peak in early to mid-summer, being largely dependent on changes in the physical, chemical and biological conditions of the water body rather than on flow, with minima in the winter. The pattern in total ammonium concentrations observed in the drier WY89 is comparable with that exhibited by NO_2^- in this year; both are similar to trends observed by Ryding & Forsberg (1979) in six Swedish rivers.

Total ORG-N concentrations range from 0.95 to 14.7 mg l^{-1} with the components varying markedly. D.ORG-N concentrations peaked in mid-summer and in wet winters. P.ORG-N concentrations peaked during the growing season in spring and summer, when nutrients undergo rapid uptake by plants. In contrast, P.ORG-N minima occurred in autumn during plant die-back.

Total nitrogen concentrations peaked in the winter corresponding with high flow and high NO_3^- concentrations. In the drier WY89, concentrations remained high in response to

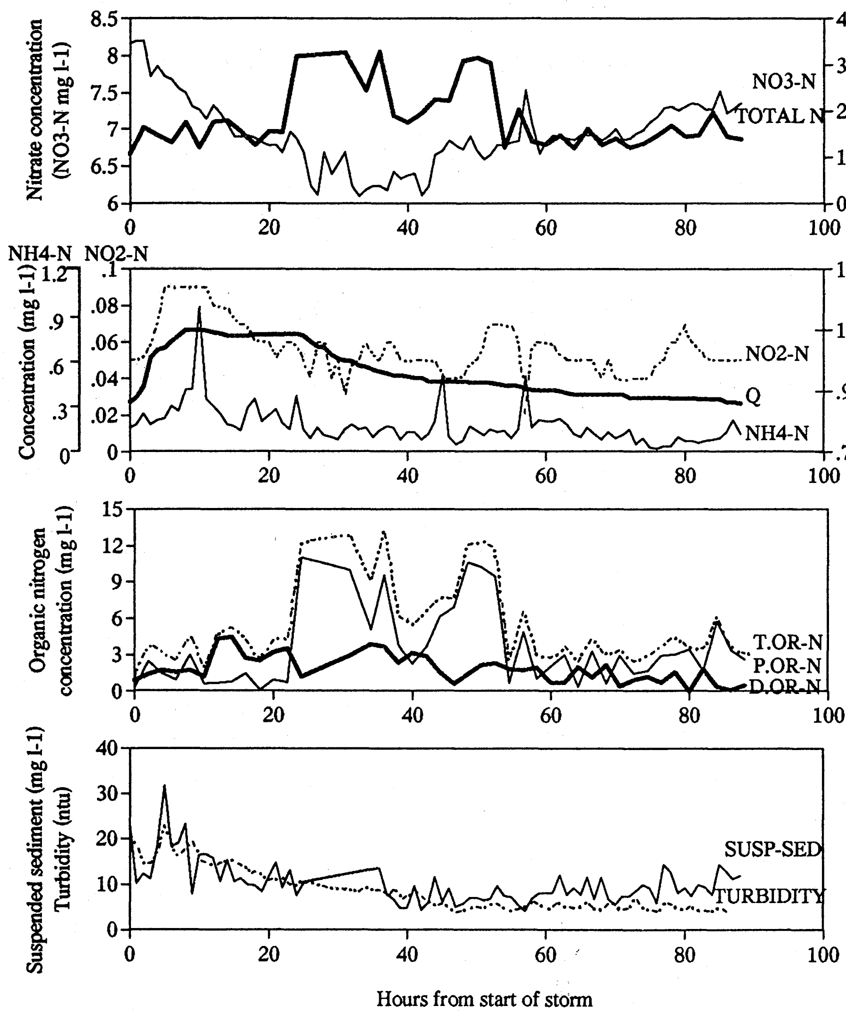

FIG. 3 Nutrient and sediment dynamics for storm of 16 September 1989.

increases in the concentrations of reduced forms of nitrogen and the ORG-N fractions, despite lower NO_3^- levels. Thus for TN, seasonality is apparent only in wetter years when NO_3^- concentrations are markedly higher in the winter. In the dry year WY89, the pattern of TN concentrations was reversed and maximum concentrations occurred in the spring and summer.

Suspended sediment concentrations vary widely at both Rissington and Worsham, but generally display a seasonal pattern with winter maxima and summer minima. Discharge and SS concentrations were statistically significant (r^2=0.13, p<0.001) for 753 observations at the Rissington site.

In summary, NO_3^-, flow, P.ORG-N, and SS all vary seasonally with maxima in January-February when the lack of crop cover on the land surface promotes leaching of solutes and erosion of sediment during storms. Nitrite concentrations peak during low flow in summer, and total ammonium and D.ORG-N peak in late summer and early autumn, corresponding with maximum mineralization rates for dead organic matter. The dominant control of SS concentrations is ambient discharge.

Storm nitrogen and sediment dynamics Several storm events were sampled at the Rissington site during WY89. The results from one event sampled on 16 September 1989, a typical late-summer storm, are presented in Fig. 3. The initial dilution of NO_3^- is followed by a rise in concentrations during the recession suggesting that NO_3^--rich soil water is delayed in reaching the river. Ammonium and NO_2^- concentrations both follow a double peaked response, with ammonium concentrations also varying in parallel with SS. The coincidence of the NO_2^- and total ammonium peaks may indicate an input of low-oxygen-content waters either from deep soil water being shunted through by new water percolating the top of the soil profile, or from effluent groundwater seepage. The ORG-N response is interesting in that, as with other storms sampled, T.ORG-N is initially dominated by D.ORG-N, being later replaced by P.ORG-N. This response was replicated for total particulate and dissolved phosphorus concentrations in several other summer storms, suggesting rapid desorption of sediment-bound nutrients once in an aquatic environment. Overall, in such summer events, the T.ORG-N contribution controls the TN response.

Annual nutrient and sediment loads

Loads were calculated for both Rissington and Worsham by interpolation from instantaneous daily concentrations and daily mean discharge, following the preferred method of Walling & Webb (method 5, table 1, 1981). Both TN and TP loads significantly decrease in a drier year at both sampling sites (Table 1). Of the TN load transported, the proportion of ORG-N increases in drier years. Ammonium loading decreases in a drier year, highlighting the importance of this contribution to storm runoff. Overall NO_3^- constitutes the greatest proportion of the TN load transported at about 60% NO_3-N, but that the total organic contribution is nevertheless significant, increasing slightly in a drier year to 40% of the total. Ammonium and NO_2^- contribute little to TN loads, but they are toxic to aquatic fauna at low concentrations. At both sites phosphate makes up the majority of the TP load at about 55%, with the relative proportions of particulate and dissolved phosphorus remaining the same from wet to dry years, perhaps highlighting the more conservative nature of the phosphorus cycle.

DISCUSSION AND CONCLUSIONS

This distributed approach to basin study has produced a full assessment of the impact of agricultural land use and land practice change upon water quality in an adjacent aquatic environment. The water sampling program provided data for the quantification of in-stream fluxes in nitrogen speciation over a range of temporal and spatial scales, an assessment of the role of sediment in nutrient cycling, and an evaluation of the proportion of individual nitrogen species contributing to the TN load.

The nitrogen speciation analyses confirm that NO_3^-, which has been the traditional focus of aquatic nutrient studies, is the single largest constituent of the TN load. Nevertheless, ORG-N contributed about 40% to the load in any one year, and concentrations were found to occasionally exceed those for NO_3^-, particularly during the summer and autumn. The mean NO_3^- concentration in WY89 was 9.2 mg l^{-1} NO_3-N with several samples exceeding the EEC limit (11.3 mg l^{-1}) during winter. Nitrate concentrations were highly correlated with flow and were significantly higher in the wetter year, whereas ORG-N concentrations were higher in the dry year. Total ammonium and NO_2^- constituted a small percentage of the total nitrogen load, but their concentrations were found to be sufficiently high to exceed established stress tolerance levels for a number of vulnerable aquatic species. Both total ammonium and NO_2^- were negatively correlated with flow.

Clearly, NO_3^- is the dominant nitrogen species contributing to the total annual nitrogen loading, with the highest NO_3^- concentrations coinciding with the highest discharge. However, other species are important to the nitrogen dynamics and transport, because these comprise almost 50% of the total nitrogen pool. This is particularly important in that nitrogen undergoes rapid interspecific cycling, with organic nitrogen contributing both to on-site and downstream inorganic nitrogen pollution.

Suspended sediment plays an important role in the delivery to and cycling of nutrients in the River Windrush. Sediment transport to surface waters was found to be an important mechanism of total ammonium, P.ORG-N and phosphorus delivery, particularly where land adjacent to the river had been ploughed or under-drained. The results suggest that, once in a river, nutrient species rapidly desorb. Furthermore, resuspension of bed sediments and erosion of bank sediments during turbulent flow effects the recycling of sediment-adsorbed nutrient fractions.

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