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DISSOLVED ORGANIC CARBON TRENDS IN SMALL STREAMS, LAND USE EFFECTS AND MODELS OF TEMPORAL VARIATION

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ABSTRACT Dissolved organic carbon (DOC) concentrations and discharge were measured in streams draining six upland Scottish catchments. Multiple regression equations of DOC on discharge and a seasonality index explained between 57 and 84% of the variance in DOC. Seasonal variations were very similar in amplitude and timing in the six streams, but discharge-related variations were least in catchments with the greatest areas of peaty soils. Mean DOC was 5-10% greater in forested catchments. A simple model of DOC, based on daily precipitation and temperature inputs, simulated mean daily concentrations in one of the streams fairly well, suggesting that changes in streamwater DOC resulting from climatic changes could be predicted relatively easily.

INTRODUCTION

Dissolved organic carbon (DOC) is a significant component of many streams, particularly those draining upland catchments with peaty soils. DOC contributes to water colour often resulting in non-compliance with drinking water quality standards (Greene, 1987). Organic complexing increases the concentrations of metals such as iron and aluminium in solution at certain times of the year (Grieve, 1990a). The negative charge associated with the organic acid radical contributes to ion balance in stream waters (Rustad *et al.*, 1986), and increased dissociation of organic acids has been shown to moderate pH increases following reductions in strong acid anion concentrations (Wright, 1989).

Seasonal variations in DOC occur in both soil (Grieve, 1990a) and stream waters (Grieve, 1984, 1990b), with a late summer maximum. Streamwater DOC concentrations also frequently increase with increasing discharge (Grieve, 1984, 1990b; Tipping *et al.*, 1988; Moore, 1989), although not always (Moore & Jackson, 1989). There have been few investigations of the catchment characteristics which control spatial variations in DOC concentrations. Data of Lock & Ford (1986) suggested that concentrations decreased with increasing stream order. Mean DOC was greater in a forested catchment at Loch Fleet in southwest Scotland (Grieve, 1990b) and, in mid-Wales, DOC concentrations in the soil solution under spruce woodland were greater than those under grassland (Reynolds *et al.*, 1988). In New Zealand, Moore (1989) and Moore & Jackson (1989) found both increased and decreased DOC concentrations when deciduous woodland was felled and replanted with pine.

The aim of this paper is to examine the role of discharge, season and catchment characteristics in controlling DOC concentrations in small streams, by comparing data from several catchments in southern and central Scotland. Based on these controls, a simple predictive model of trends in streamwater DOC is formulated and evaluated.

FIELD SITES AND ANALYTICAL METHODS

Data from six Scottish catchments were used in this study, one catchment in the Ochil Hills 20 km north of Stirling in central Scotland, two catchments in the Aberfoyle area some 40 km north of Glasgow and three subcatchments of the Loch Fleet catchment in southwest Scotland. Area, altitudinal range, vegetation and sampling dates for each catchment are given in Table 1. Soils in all six catchments were dominantly peat (Histosol) or had peaty (histic) horizons. Only the Ochil catchment had a significant area of mineral soils, with 25% of the catchment area mapped as brown forest soil (Cambisol). Samples for DOC analysis were obtained at 8 h intervals in the Ochils catchment for the entire duration of the sampling period indicated in Table 1, at 4 or 8 h intervals for most of the sampling period in the Loch Ard catchments and at 1 or 2 h intervals during storm events in the Loch Fleet catchments. DOC was determined by wet oxidation, from absorbance at 360 nm, or by TOCSIN aqueous carbon analyser. Calibration of the different methods against one another indicated close agreement with no evidence of bias. Stream discharge was obtained from continuous records.

TABLE 1 Characteristics of the catchments studied.

Catchment	Area (ha)	Altitude (m)	Vegetation	Sample dates
Fleet 4	4.9	340-390	Spruce/pine forest	4/86-4/88
		planted 1961.		
Fleet 6	4.2	340-400	Grass/heather moor	4/86-4/88
Fleet 7	40	340-470	Grass/heather moor	4/86-4/88
Ard 10	84	105-220	Spruce/pine forest	9/89-5/90
		70% cleared in 1988		
Ard 11	151	100-280	Spruce/pine forest	9/89-5/90
Ochil	51	260-470	Grass/heather moor	6/82-6/83

SEASONAL AND HYDROLOGICAL VARIATIONS

DOC concentrations in all six streams were positively correlated with discharge, with maximum DOC during storm events. Figure 1 shows the variation in DOC during one week in October 1989 in the streams draining the two Loch Ard catchments. In both catchments the relationship between discharge and DOC was very close, although evidence from the Fleet catchments indicated that maximum DOC concentrations occurred shortly after maximum discharge. The amplitude of variation of DOC was greater in the clear-felled catchment (Ard 10). This pattern of variation in DOC with changing discharge during storm events was typical of all of the catchments examined.

The close relationship between DOC and discharge within individual storm events was not immediately evident when DOC was regressed on discharge over the entire sampling period at each site. The largest values of R^2 were obtained when DOC was regressed on log(Q), but these ranged from 0.2 to 0.5. Examination of the residuals from the regression equations indicated significant seasonal cycles in all six cases, similar to that reported by Grieve (1984) for the Ochil catchment. The seasonal variation was included in multiple regression equations as an annual sine wave with maximum in late summer.

The regression equations for the six catchments are listed in Table 2. All equations were statistically significant, with log(Q) and the seasonal curve explaining between 57 and 84% of the variance in DOC. The sine curves for all six streams had maxima in August, normally the month of maximum soil and air temperature, and the coefficients of the sine index ranged from 3.2 to 4.4.

Table 2 shows a remarkable degree of similarity in both the timing and amplitude of the seasonal variation in DOC within the six catchments, indicating the important role that temperature plays in the release of soluble organic materials within catchments.

The variation in DOC with discharge was much less consistent among the catchments. Regression coefficients for log(Q) ranged from 0.8 to 5.4. Smaller slopes indicate catchments where there was little variation in DOC concentration with flow, as comparison of short-term DOC variations at Ard 10 and Ard 11 (Fig. 1) confirms. Large variations in DOC with discharge are probably related to difeerences with depth in mineral soils. At low flow water is derived from lower horizons of the soil, and, in mineral soils, these have smaller DOC concentrations. McDowell & Wood (1984) found a mean DOC concentration of 33 mg l^{-1} in soil water from the A2 horizon of a New Hampshire podzol and 2-3 mg l^{-1} in subsoil waters. In catchments with dominantly mineral soils, streamwater DOC might thus be expected to vary significantly between low and high flows. In peaty soils in the Loch Dee catchment in southwest Scotland, Grieve (1990a) found relatively little difference between soil water DOC from upper and lower soil horizons, and Moore (1987) reported a similar lack of DOC variation with depth in Canadian peatlands. In such

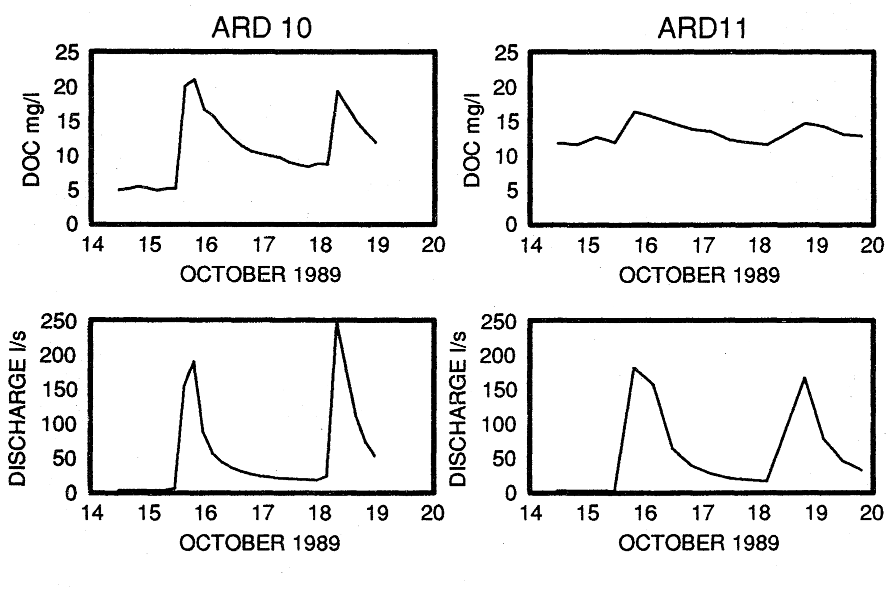

FIG. 1 Variations in DOC and discharge during one week in October 1989 at Ard 10 and Ard 11.

catchments there should be less variation in DOC with flow. Of the catchments examined here, Ochil had the greatest percentage of mineral soils, with brown earths at low elevations and peat only occurring on 25% of the catchment area. The largest regression coefficient for log(Q) was found in this stream. Soil cover in the Loch Fleet catchments was dominated by peat (70% of catchment area, with the other 30% mostly peaty mineral soils), and regression coefficients for log(Q) were smallest. At Loch Ard, catchment 10 had steeper slopes and, although soils of the catchment have not been mapped in detail, probably a larger proportion of mineral soils than catchment 11. The larger regression coefficient for Ard 10 would be consistent with such a difference.

TABLE 2 Regressions of DOC on log(Q) and seasonality index (SI) for the six streams. DOC is dissolved organic carbon in mg l^{-1}, Q is discharge in l s^{-1}, and SI is a seasonal sine index with maximum in August. Standard errors of the regression coefficients are given in parentheses.

Fleet 4:	DOC = 8.6 + 2.1 log(Q) + 3.9 SI (0.2) (0.3) (0.2)	$R^2 = 0.58$
Fleet 6:	DOC = 7.9 + 0.8 log(Q) + 4.4 SI (0.2) (0.2) (0.2)	$R^2 = 0.72$
Fleet 7:	DOC = 2.8 + 2.7 log(Q) + 3.6 SI (0.4) (0.2) (0.2)	$R^2 = 0.57$
Ard 10:	DOC = 2.3 + 3.9 log(Q) + 3.2 SI (0.3) (0.2) (0.1)	$R^2 = 0.58$
Ard 11:	DOC = 6.6 + 1.7 log(Q) + 3.5 SI (0.2) (0.1) (0.1)	$R^2 = 0.84$
Ochil:	DOC = -2.5 + 5.4 log(Q) + 3.2 SI (0.2) (0.1) (0.1)	$R^2 = 0.82$

CATCHMENT LAND USE EFFECTS

Differences in the effects of forest and moorland vegetation on streamwater DOC concentrations can be gauged from the Ard and Fleet sites. Ard 10 had a near 100% cover of pine and spruce prior to January 1988, but was 70% clearfelled between this date and the beginning of sampling in September 1989. Ard 11, the control catchment for the clearfelling experiment in Ard 10, had a near 100% cover of 30 year old conifers for the duration of the sampling period. Fleet 4 had an 88% cover of 15 year old Sitka spruce and Lodgepole pine. Comparison of Fleet 4 with the 40 ha Fleet 7 catchment is probably not valid, given the decrease in mean DOC concentrations with increasing catchment size (Lock & Ford, 1986). Fleet 6, however, had a similar area to that of Fleet 4 and 100% moorland vegetation cover. Means and standard deviations for DOC concentrations in the streams draining the four catchments are given in Table 3. At both sites the mean DOC was significantly greater ($p<0.01$) in the forested stream. Calculation of discharge-weighted mean DOC (Table 3) indicated, however, that the absolute differences between the catchment pairs were small, between 5 and 10% of mean DOC.

TABLE 3 Mean DOC concentrations in forested and non-forested catchments.

	Ard 10 felled	Ard 11 forest	Fleet 6 moorland	Fleet 4 forest
Mean DOC (mg l^{-1})	7.6	9.2	10.1	10.8
Standard deviation	3.2	2.8	2.7	2.5
Sample size	560.	322.	208.	212.
Discharge-weighted mean DOC (mg l^{-1})	8.8	9.2	9.8	10.8

Whether such a difference is due solely to the presence or absence of a forest cover or to minor differences in soil types or slopes between the catchment pairs must be a matter of conjecture, and confirmation of the magnitude of any effect requires comparison of a larger number of paired forest and non-forest catchments. However, previous research has established that forests can alter the nature and thickness of soil organic horizons (Miles, 1985) and the proportions of water flowing through different soil horizons (Hornung & Newson, 1986). Mobile organic compounds are also released into the soil as canopy drip under forests (Malcolm & McCracken, 1968). Spruce forest was thus associated with larger mean DOC in the soil solution than acid grassland vegetation (Reynolds *et al.*, 1988). However, on the basis of the evidence here any catchment-scale effect of afforestation on streamwater DOC is likely to be small.

MODEL OF DOC VARIATIONS

The relatively simple hydrological and seasonal effects identified above suggested that it was possible to model variations in DOC concentrations in upland catchments using a limited number of temperature-related decomposition parameters to describe production and decomposition of soluble organic carbon in a leaching model. Such a model, based on the hydrology of the Birkenes model (Christophersen & Wright, 1981), has been formulated and applied to soil solution DOC variations at Loch Dee in southwest Scotland and to prediction of variations in streamwater DOC from the Ard 10 catchment during storm events in October 1989 (Grieve, in press).

The DOC submodel identified two stores of soluble carbon in the soil, corresponding to the two soil layers in the hydrological model. These carbon stores determined the DOC concentrations in water draining from them, as a fixed proportion of soluble carbon in each store. Carbon was added to the upper store by a temperature-controlled decomposition process acting on carbon in the soil, similar to the empirical model of CO_2 release formulated by Anderson (1973). The total carbon in the soil was assumed not to change during the simulation period. Carbon was added to the lower store as DOC in drainage water from the upper store. Carbon in both stores was lost by decomposition, as a first-order decay process. Model parameters were not optimised against measured DOC concentrations, but initial stores of soluble carbon, and decomposition parameters were selected to be consistent with known rates of organic matter decay in the soil (Jenkinson & Rayner, 1977). Full details of the model and parameter selection are given by Grieve (in press).

The model was used here to predict mean daily discharge and DOC concentrations over a nine month period in the stream draining the Ard 10 catchment. Daily precipitation totals were obtained from a raingauge at the catchment gauging station, and daily temperatures from a meteorological station at Aberfoyle, some 4 km from the catchment. Predicted and measured mean daily stream discharges between August 1989 and April 1990 are shown in Fig. 2. Most of the peaks in discharge during the period are predicted by the model, but many of the predicted peaks occurred one day later than the corresponding measured peak. This is a direct consequence of using daily precipitation totals to drive the model, a point made with reference to the same hydrological model by Christophersen & Wright (1981).

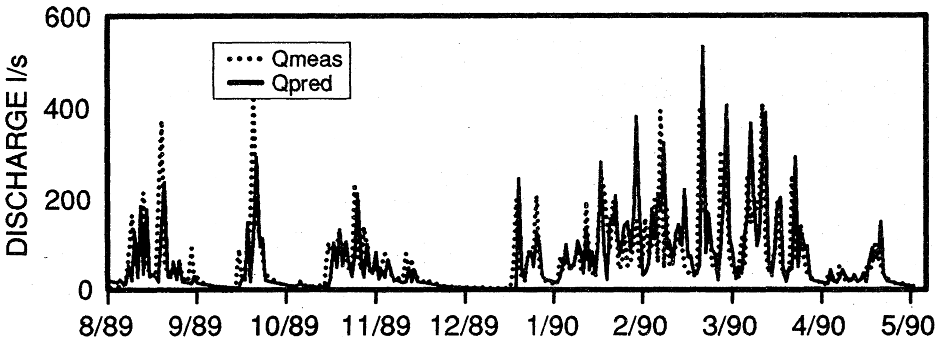

FIG. 2 Predicted and measured discharge in the Ard 10 stream between A gust 1989 and April 1990.

Predicted and measured mean daily DOC are shown in Fig. 3. Given the rather preliminary nature of the model, agreement between measured and predicted DOC was assessed by visual comparison. Agreement was good for the autumn DOC peaks occurring during September and October 1989, and the declining concentrations during early November and January/February also were well predicted. Increased DOC concentrations during April 1990 were identified, but the model failed to predict the measured increase during March 1990. Regression of measured concentrations on predicted concentrations for the entire period yielded the equation:

$$DOC_{meas} = 4.2 + 0.59\ DOC_{pred} \qquad r^2 = 0.50$$

This equation is consistent with overprediction by the model of large DOC concentrations, but underprediction of smaller concentrations.

The overall performance of the model during the test period was thus encouraging, especially in view of the fact that the organic matter addition and decomposition parameters in the model were not optimised but were selected as physically realistic values based on

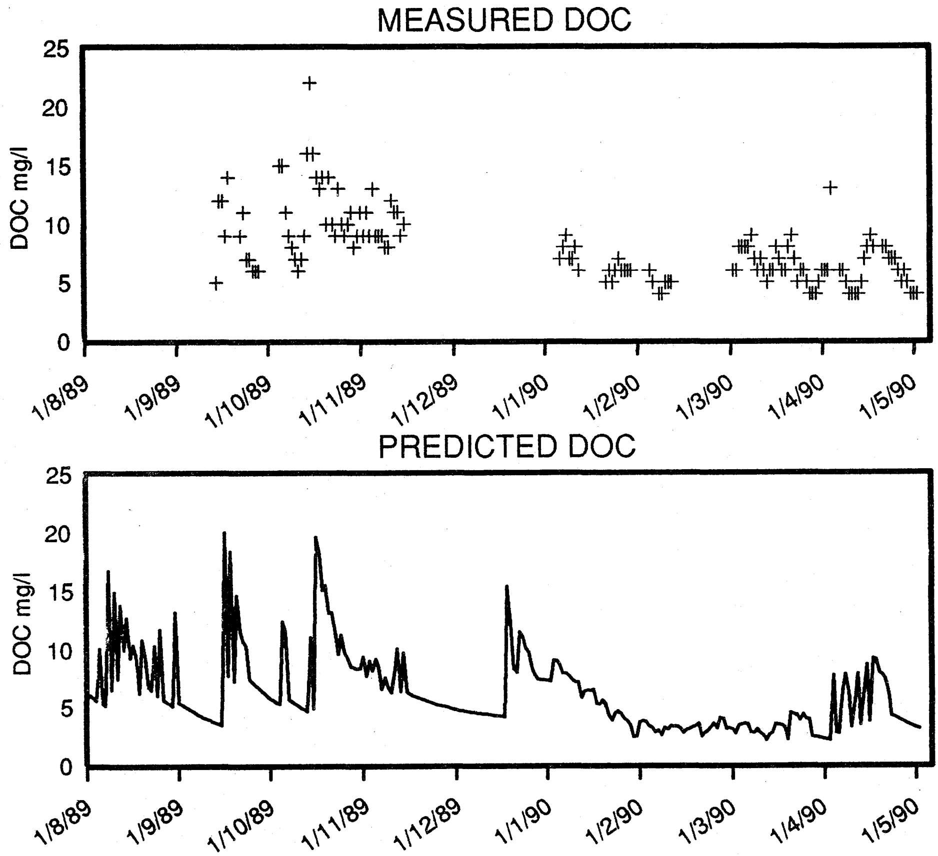

FIG. 3 Predicted and measured DOC in the Ard 10 stream between August 1989 and April 1990.

previous studies of organic matter decomposition. Further refinement of the model is clearly required, including sensitivity analysis and optimisation of the model parameters and testing of the resultant predictions. Such refinement requires a data set for the catchment of at two or three years, to ensure the stability of the carbon stores in the model on an annual basis. A fully calibrated model would be of greatest value in predicting changes in streamwater DOC concentrations, and hence colour, which would result from higher average temperature or different rainfall amounts or distribution. A more realistic model in this context would also need to include a model of changing total carbon content in the soil, and a quantitative treatment of the effect of changes in the total soil carbon on the soluble carbon stores.

CONCLUSIONS

Dissolved organic carbon concentrations in streamwater vary both with discharge and seasonally. Discharge-related variations depend on soil conditions in the stream catchment area, and were less pronounced in streams draining catchments with peaty soils. Seasonal variations were consistent among a range of catchments in Scotland. The two forested catchments studied had slightly (5-10%) greater mean DOC concentrations. A simple model of DOC based on precipitation and temperature inputs predicted DOC satisfactorily in one of the catchments.

Increased concentrations of dissolved organic compounds have significant implications for water colour, for acidity, and for metal complexation. These implications suggest that factors such as climatic change and of catchment afforestation which affect streamwater DOC require further investigation, specifically to quantify the magnitude of DOC changes resulting from changes in these factors.

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