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RELATIONSHIP BETWEEN CATCHMENT CHARACTERISTICS AND NUTRIENT CONCENTRATIONS IN AN AGRICULTURAL RIVER SYSTEM

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Abstract—We examined the effects of catchment characteristics and riverine processes on the concentrations of nutrients and total suspended solids (TSS) using data from the outlets of 12 tributaries (9–139 km^2) and 22 main channel sites of a river draining an intensely cropped area of 1088 km^2 in SW Finland. For the tributaries, the flow-weighted mean concentrations of TSS and total phosphorus (TP), which both reflect erosion, were best explained by field percentage and the mean slope of the fields of the catchment. The best model describing the concentration of dissolved reactive P (DRP) included field percentage and catchment area. Total nitrogen (TN) and nitrate + nitrite-nitrogen (NO_x-N) correlated only with field percentage. Except for DRP, the regression models derived from the tributary data rather accurately predicted the concentrations in the main river channel. Our results suggest that, with regard to lakeless catchments of 10–1000 km^2, the export of TP, TSS and N per unit area remains constant. Furthermore, although some P in eroded soil particles may be released into dissolved, algal-available form during the river transport, erosion control appears not to efficiently reduce dissolved P. © 2000 Elsevier Science Ltd. All rights reserved

Key words—eutrophication, agriculture, nutrients, rivers

INTRODUCTION

Agricultural nutrient losses have been demonstrated to accelerate eutrophication of aquatic systems in many countries. In Finland, crop production areas are located mainly in the southern parts of the country, where the most severe eutrophication problems of lakes and coastal waters are also encountered (Kauppi *et al.*, 1993). To abate the eutrophication, efficient loss reduction measures should be implemented in agricultural catchments. However, their implementation is confounded by the fact that the nutrient losses, particularly those of P, are not evenly distributed within agricultural land but show a wide spatial variation according to soil characteristics, topography, climate and agricultural practices (Mansikkaniemi, 1982; Rekolainen and Leek, 1996; Pionke *et al.*, 1997). Furthermore, not all nutrients leaving the edge of a field will reach a body of water susceptible to eutrophication, but may be retained during transport (Walling 1977; Prairie and Kalff, 1986; Arheimer and Brandt, 1998). The retention has been reported to increase with catchment size, resulting in a spatial "scale effect" of observed nutrient losses per unit area (Walling, 1977; Prairie and Kalff, 1986). Furthermore, all forms of nutrients are not available to algae and thus do not contribute to the eutrophication (Ekholm, 1994). Varying conditions during transport may affect the partitioning of nutrients between dissolved and particulate phases (Green *et al.*, 1978; Logan, 1982), which can influence the availability of nutrients and consequently their eutrophying effect. In conclusion, the measures to reduce nutrient losses from crop production areas should particularly be directed towards the catchments contributing most to the actual loading (absolute loss minus retention) of algal-available nutrients.

The aim of this study was to test whether readily available data on catchment characteristics can be used to identify catchments with high loading potential. This was accomplished by examining the relationship between the mean concentration of nutrients and total suspended solids (TSS) and (i) field percentage, (ii) mean slope of the fields and (iii) catchment area in small agricultural catchments within a river system (the River Paimionjoki) located in an intensely cultivated region of SW Finland. We examined concentrations instead of losses,

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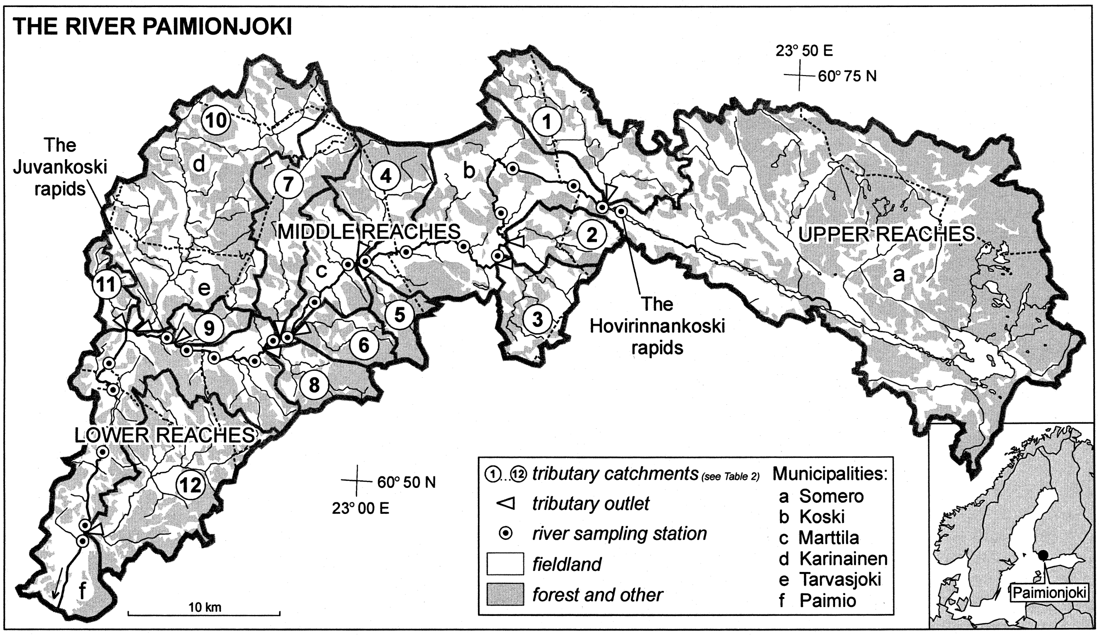

Fig. 1. The River Paimionjoki and the tributary catchments.

because there were no spatial flow data for the catchments. The second aim was to estimate the net effects of riverine processes during the transport using data from the main river channel.

MATERIALS AND METHODS

Study site

A total of 43% of the drainage basin of the River Paimionjoki (1088 km^2) is agricultural land, mainly under crop production, whereas the remaining area consists of forests (50%), peatland (4%) and lakes (1.5%, Fig. 1). The topsoil of agricultural land is mostly clayey, although even moraine exists in some fields (Table 1). Erosion of surface soil of fields makes the river and tributary waters turbid, especially during high flow (Mansikkaniemi, 1982; Pietiläinen and Ekholm, 1992). Most of the annual flow and nutrient transport occurs during the snowmelt in spring—occasionally also in winter—and during autumn storms (Ekholm and Kallio, 1996); at dry periods in summer, there is almost no flow in the river. The seasonal variations in the flow are accentuated by several factors: (i) rain and snowmelt water from the predominantly fine-textured agricultural land is rapidly transported to streams as surface runoff or via subsurface drainage due to preferential flow; (ii) the water storage capacity of forest land is relatively low due to a high number of bedrock outcrops; and (iii) there are only a few lakes and reservoirs to store excess water.

Five municipalities discharge purified effluents into the River Paimionjoki. Most of the wastewater load originates from the municipality of Paimio and is discharged at the outlet of the river. Excluding this impacted area (accounting for 2% of the whole drainage basin), 85% of the anthropogenic P and 87% of the N loading to the river originates from field cultivation, 8% of P and 6% of N from animal husbandry (e.g. losses of nutrients in silage liquor and from manure storage) and 5% of P and 3% of N from the sparse population of about 8000 persons (Ekholm, unpublished data).

In total, there are six municipalities in the drainage basin of the River Paimionjoki (Fig. 1). In Finland, most statistics on agriculture are available only from municipalities, which inhibits detailed estimation of the regional differences. The P status of topsoil, analysed by acid ammonium acetate extraction, increased from 7.3 mg l^{-1} in the municipality of Somero in the upper reaches of the river to 13.9 mg l^{-1} in the municipality of Paimio in the lower reaches (Table 1). According to the agricultural census of 1990 (data provided by the Ministry of Agriculture and Forestry), spring crops (mainly barley, oats, wheat, rape) were cultivated in 65–72% of the field area. In the

Table 1. Agricultural statistics by municipalities in the River Paimionjoki

Municipality	Catchment	P-status[a] (mg l^{-1})	Dominant soil types of fields[b]	Livestock[c] (units ha^{-1})
Somero	1, 2	7.3	sandy, gyttja and loam clay; finer fine sand	0.35
Koski	1, 2, 3, 4, 5	8.9	heavy, gyttja, loam and sandy clay; finer fine sand	0.32
Marttila	4, 5, 6, 7, 8, 9	8.2	gyttja, sandy and silty clay	0.32
Karinainen	7, 10	10.3	gyttja and sandy clay; finer fine sand	0.34
Tarvasjoki	9, 10, 11, 12	10.0	sandy and gyttja clay; finer fine sand	0.36
Paimio	12	13.9	sandy, silty and gyttja clay; finer fine sand	0.29

[a]Given as mg P per 1 l of dry soil. Based on acid ammonium acetate extraction (Vuorinen and Mäkitie, 1955) of surface soils performed in soil fertility analyses during 1981–1985 (Kähäri *et al*., 1987) and 1986–1990 (Viljavuuspalvelu Oy, unpublished data).
[b]Based on Kähäri *et al*. (1987) and Viljavuuspalvelu Oy (unpublished data).
[c]Based on the agricultural census of 1990 (Data provided by the Ministry of Agriculture and Forestry).

municipality of Paimio, the proportion of spring crops was lowest and that of winter crops (mainly wheat, rye) highest (19%, in the other municipalities 11–15%). The proportion of both grassland and fallow ranged from 6 to 8% and that of total winter greens from 25 to 31% (highest in Paimio). The number of livestock units per hectare of field varied from 0.29 to 0.36, being lowest in Paimio (Table 1).

The area above the Hovirinnankoski rapids (373 km^2), hereafter referred to as the upper reaches, forms a distinct river section, characterized by a relatively low proportion of fields (35%) and some "larger" lakes (lake percentage 4.5), regulated to ensure water abstraction in the lower reaches. In the present study, the focus was on the intensely cultivated (field percentage 47), almost lakeless area below the Hovirinnankoski rapids (715 km^2). This section was divided into the middle reaches (above the Juvankoski rapids), dominated by relatively flat agricultural plains, and the lower reaches with more undulating topography and markedly higher erodibility (Mansikkaniemi, 1982). The mean slope of the fields in the middle and lower reaches was 0.9%, a typical value for this part of the country (see Rekolainen, 1993). From this section, 12 tributary catchments ranging from 9 to 139 km^2 and having 23–62% of agricultural land were chosen for closer examination (Fig. 1, Table 2). In total, these tributaries accounted for 44% of the whole drainage basin and for 66% of the middle and lower reaches.

Catchment characteristics

The locations and areas of cultivated fields were derived from the land use data provided by the National Land Survey of Finland. These data have a resolution of 25 × 25 m and are based on satellite images enhanced by agricultural areas digitised from 1:50,000 topographic maps. Slope distribution of agricultural areas was estimated by two methods. First, it was approximated manually from the topographic maps by dividing the catchments into 500 × 500 m grids. On the basis of the elevation contours, the steepest section of agricultural land in each grid was identified and its slope was determined by dividing the distance between the contours by the difference in altitude. Second, the slope was calculated from a digital elevation model (DEM) provided by the National Land Survey. The DEM is based on the digitised contour lines of the 1:10,000 topographic map with contour intervals of 5 or 2.5 m. To obtain a slope value, the difference in altitude of each 25 × 25 m grid from all its neighbouring grids in the agricultural area was determined. This difference was divided by the distance between the centre of the processing grid and each of the neighbouring grids (see Kallio *et al*., 1997). The mean slopes obtained by both methods correlated with each other ($r^2 = 0.81$, $p < 0.01$), but those estimated manually were twice as high as those given by DEM, which is reasonable since the manual method focused on the steepest fields. Only the DEM data (given in Table 2 for the tributaries) were used later on. The available spatial data on soil types were not used here, since the grid size (200 × 200 m) of the data was considered too scarce. In addition, these data were based on the mapping of the quaternary deposits, which inaccurately reflects the soil texture.

Table 2. Characteristics of the tributary catchments in the River Paimionjoki

No.	Name	Catchment		
		Area (km^2)	Fields (%)	Mean slope of the fields (%)
1	Palojoki	57.6	55	0.6
2	Halliniitunoja	22.7	57	0.7
3	Pahonoja	28.2	52	0.9
4	Hirvasoja	32.8	37	0.7
5	Lapinoja	13.9	23	0.8
6	Lappalaistenoja	15.6	31	0.9
7	Ihmistenoja	45.7	47	0.5
8	Hallinoja	20.3	28	0.7
9	Särkisuonoja	9.2	62	0.6
10	Tarvasjoki	139.1	48	0.8
11	Rasunoja	11.1	46	1.2
12	Vähäjoki	77.6	38	1.2
Mean		39.5	44	0.8

Sampling and analysis of water samples

During 1989–1994, a total of 20 sampling surveys on water quality were conducted. During these surveys, water samples were taken from the 12 tributary outlets and from 22 sites in the main river channel, located predominantly before and after the outlet of each tributary (Fig. 1). Surveys were mostly conducted during wet periods (spring and autumn), and consequently the mean flow of the sampling days was twice as high as the mean flow during the whole study period (Table 3). However, a few surveys were also performed at low-flow periods in summer and winter, and occasionally some of the outlets were dry at the time of sampling.

The samples were analysed for TSS, total P (TP), dissolved reactive P (DRP), total N (TN), ammonium-N (NH_4-N), nitrate + nitrite-N (NO_x-N), conductivity, temperature and pH. Total suspended solids were determined gravimetrically according to the European standard EN872 (Finnish Standards Association SFS, 1996), except for the filters used. In addition, contrary to the recommendation of the standard, the filtration time was allowed to exceed 1 min. Dissolved reactive P was analysed from filtered samples using the molybdate blue method (Murphy and Riley, 1962). In TP determination the sample was digested by potassium peroxodisulphate before analysis with ammonium molybdate. Ammonium nitrogen was analysed colorimetrically with hypochlorite and phenol and NO_x-N was analysed by reduction of NO_3^- (Hg–Cd or Cu–Cd) followed by NO_2^- determination. Total nitrogen was analysed as NO_3^- after digestion of the sample with peroxodisulphate. In all filtrations, Nuclepore polycarbonate membranes with 0.4 μm pore size were used.

Analysis of the data

For all sampling sites, flow-weighted mean concentrations ($\bar{c}$) of TSS, TP, DRP, TN, NH_4-N and NO_x-N were calculated as follows:

$$\bar{c} = k \frac{\sum_{d=1}^{n} c_d Q_d}{\sum_{d=1}^{n} Q_d} \quad (1)$$

where c_d is the concentration on day d (μg or mg l^{-1}), Q_d the flow at Juvankoski rapids on the same day ($m^3\ s^{-1}$), n the number of observations (≤ 20) and k the conversion

Table 3. Mean, minimum and maximum daily flows ($m^3\ s^{-1}$) at the Hovirinnankoski and Juvankoski rapids in the River Paimionjoki

Period	Hovirinnankoski			Juvankoski		
	Mean	Min	Max	Mean	Min	Max
1989–1994	2.6	0.0	14.0	7.2	0.0	87.6
Sampling days	3.5	0.3	11.2	14.9	0.7	57.4

factor for units. Daily flow data was available only for the Hovirinnankoski and Juvankoski rapids (the Hydrological Data Base of the Finnish Environment Institute). Since the sampling sites were located in a relatively restricted area, the flow at Juvankoski may be assumed to represent reasonably well the temporal flow variations at all sites. Hereafter, mean concentration refers to the flow-weighted mean concentration.

The mean tributary concentrations were explained by three catchment characteristics: field percentage, mean slope of the fields and area of the tributary catchments. The statistical analyses were facilitated by the fact that the mean tributary concentrations were normally distributed (Shapiro–Wilk test). In addition, the explaining variables did not correlate with each other. At first, the data were explored by two multivariate analyses: a common factor analysis and a canonical correlation analysis. The factor analysis, performed on the correlation matrix of the mean tributary concentrations, revealed two common factors (with eigenvalue exceeding 1). Factor 1 comprised of TN, NO_x-N, DRP, NH_4-N and TP (listed in a decreasing order of factor loading). Factor 2 was formed primarily by TSS and TP. These two factors might be interpreted to reflect (1) nutrients mostly in a dissolved form and (2) eroded particulate matter, respectively. Among the tributaries, the score of Factor 1 ("dissolved nutrients") tended to increase with field percentage. On the other hand, tributaries 11 and 12, with the most inclined fields, had clearly the highest scores for Factor 2, which suggested that mean slope reflected the erosivity of the tributaries. Canonical correlation analysis supported this interpretation. It revealed two noteworthy canonical correlations ($p = 0.01$ and $p = 0.07$). The first canonical variable for the catchment characteristics was a weighted difference of slope + field percentage and drainage basin area, with most emphasis on slope. Of the mean concentrations, those of TSS and TP (+ NH_4-N) correlated with the first canonical variable. The second canonical variable was a sum of field percentage (most weight) and catchment area. All mean concentrations correlated with this variable, TSS having the lowest correlation.

The effect of catchment characteristics on the mean tributary concentrations was further studied by simple regression models and Pearson product-moment correlations. A level of $p < 0.05$ was used as a minimum level for a significant correlation. In addition, stepwise regression models for a combination of explaining variables were calculated. All variables left in a stepwise regression model were significant at the 0.15 level (the procedure was also performed using a significance level of 0.1, but with no effect on the results). All statistical analyses were made using SAS software (SAS Institute Inc., 1989, 1990).

Provided that there is no scale effect, the regression models derived from the tributary data should in theory also predict the mean concentrations in the main river channel. To test this hypothesis, the concentrations in the river channel were predicted using the regression model with the highest r^2-value for a particular water quality variable, except for the models with catchment area as an explaining variable. However, as there were lakes retaining nutrients in the river section above the Hovirinnankoski rapids (the upper reaches), the quality of water coming from this area could not be predicted using the regression models concerning almost lakeless tributaries. Instead, it was assumed that the mean concentration at a river channel site i was a mixture of water originating from the upper reaches and of water coming from the drainage basin between Hovirinnankoski and site i. The "mixing ratio" was obtained from the proportions of drainage basin area and mean runoff of the upper reaches and of the lower area. Thus, the mean concentration (c_i) at river channel site i was obtained as follows:

$$c_i = \frac{A_H \times q_H \times c_H + A_i \times q_i \times c_{pi}}{A_H \times q_H + A_i \times q_i} \quad (2)$$

where A_H and A_i are the drainage basin areas of the upper reaches and the area between Hovirinnankoski and site i, respectively, q_H and q_i the mean runoff in these two areas, c_H the mean concentration in the water at Hovirinnankoski and c_{pi} the mean concentration predicted by regression models for the water originating below the Hovirinnankoski.

The fit between the observed and predicted mean concentrations was judged using the model efficiency criterion (R_0^2, Nash and Sutcliffe, 1970), based on the ratio of initial variance (F_0^2) and residual variance (F^2):

$$R_0^2 = \frac{F_0^2 - F^2}{F_0^2}, \quad (3)$$

$$F_0^2 = \sum_{i=1}^{n} (\text{obs}_i - \text{obs}_m)^2, \quad F^2 = \sum_{i=1}^{n} (\text{obs}_i - \text{pred}_i)^2 \quad (4)$$

where obs_i is the observed mean concentration of the ith site, obs_m is the arithmetic mean of the observations for all sites, pred_i is the calculated mean concentration for the site and n is the number of sites. The values for R_0^2 range from minus infinity to +1; +1 indicates complete agreement between the observed and calculated values.

RESULTS

Concentrations in the tributary outlets

The mean concentrations of TP in the tributary outlets ranged from 190 to 440 $\mu g\ l^{-1}$ and those of TSS from 140 to 350 mg l^{-1} (Fig. 2). As indicated by the strong correlation between TP and TSS ($r^2 = 0.95$, $p < 0.001$), most of the P was in a particulate form; the mean concentrations of DRP were only 13–42 $\mu g\ l^{-1}$. The concentrations of TP, TSS as well as DRP appeared to increase with the field percentage of the tributary catchment, although in the case of TSS the correlation with field percentage was insignificant (Fig. 2, Table 4). The two tributaries with most inclined fields (nos 11 and 12) exhibited higher concentrations of TP and TSS than suggested by their field percentage alone (46 and 38, respectively). Accordingly, regression models including the mean slope of the fields, in ad-

Table 4. Regression models ($p < 0.05$) between the flow-weighted mean concentrations of water quality variables ($\bar{c}$) and catchment characteristics[a]

Variable	Unit	Model	r^2	p
TP	$\mu g\ l^{-1}$	$\bar{c} = 3.49 \times Fi + 149$	0.33	< 0.05
		$\bar{c} = 4.93 \times Fi + 245 \times Sl - 108$	0.89	< 0.001
TSS	mg l^{-1}	$\bar{c} = 178 \times Sl + 74$	0.51	< 0.01
		$\bar{c} = 3.07 \times Fi + 227 \times Sl - 99$	0.89	< 0.001
DRP	$\mu g\ l^{-1}$	$\bar{c} = 0.59 \times Fi + 4.56$	0.55	< 0.01
		$\bar{c} = 0.55 \times Fi + 0.09 \times A + 2.34$	0.69	< 0.01
TN	$\mu g\ l^{-1}$	$\bar{c} = 47.2 \times Fi + 1052$	0.67	< 0.01
NO_x-N	$\mu g\ l^{-1}$	$\bar{c} = 44.8 \times Fi + 133$	0.62	< 0.01
NH_4-N	$\mu g\ l^{-1}$	$\bar{c} = 0.93 \times A + 54$	0.63	< 0.01

[a] Fi = field percentage (%), Sl = mean slope of the fields (%), A = area of a catchment (km^2), r^2 = coefficient of determination, n = 12.

dition to field percentage, best explained the mean concentrations of TP and TSS (for both variables: $r^2 = 0.89$, $p < 0.001$, Table 4). Total suspended solids was the only variable which correlated solely with slope ($r^2 = 0.51$, $p < 0.01$). The model best explaining DRP included field percentage and catchment area but had a lower r^2-value (0.69, $p <$ 0.01) than the best models for TP and TSS. Catchment area was included in the model due to the fact that the mean DRP concentration was low in the smallest tributary (no. 9), which had the highest field percentage (62).

The mean concentrations of TN ranged from 2100 to 4400 μg l^{-1} (Fig. 2). Nitrogen was mostly in the form of NO_x-N, which ranged from 1200 to 3400 μg l^{-1}. The only catchment variable explaining the concentrations of TN and NO_x-N was field percentage (Table 4). Tributary 9 with low DRP concentrations also had lower N concentrations than suggested by field percentage (Fig. 2). The mean concentrations of NH_4-N (18–160 μg l^{-1}) correlated only with catchment area.

Concentrations in the river channel

In the main river channel, the mean observed concentrations of TSS and TP behaved in a similar way: the concentrations were lowest at the uppermost sampling site (the Hovirinnankoski rapids), reflecting the relatively low field percentage (35) of the upper reaches and the possible retention of eroded soil particles by the lakes in this river section. However, within an intensely cultivated (field percentage 56) river section of 200 km^2, located immediately below Hovirinnankoski, the concentrations of TSS doubled and those of TP also increased substantially. In the lower reaches of the river, field percentage gradually decreased to 40 and the concentrations of TSS and TP levelled off but peaked at the sampling site closest to the river mouth (Fig. 3).

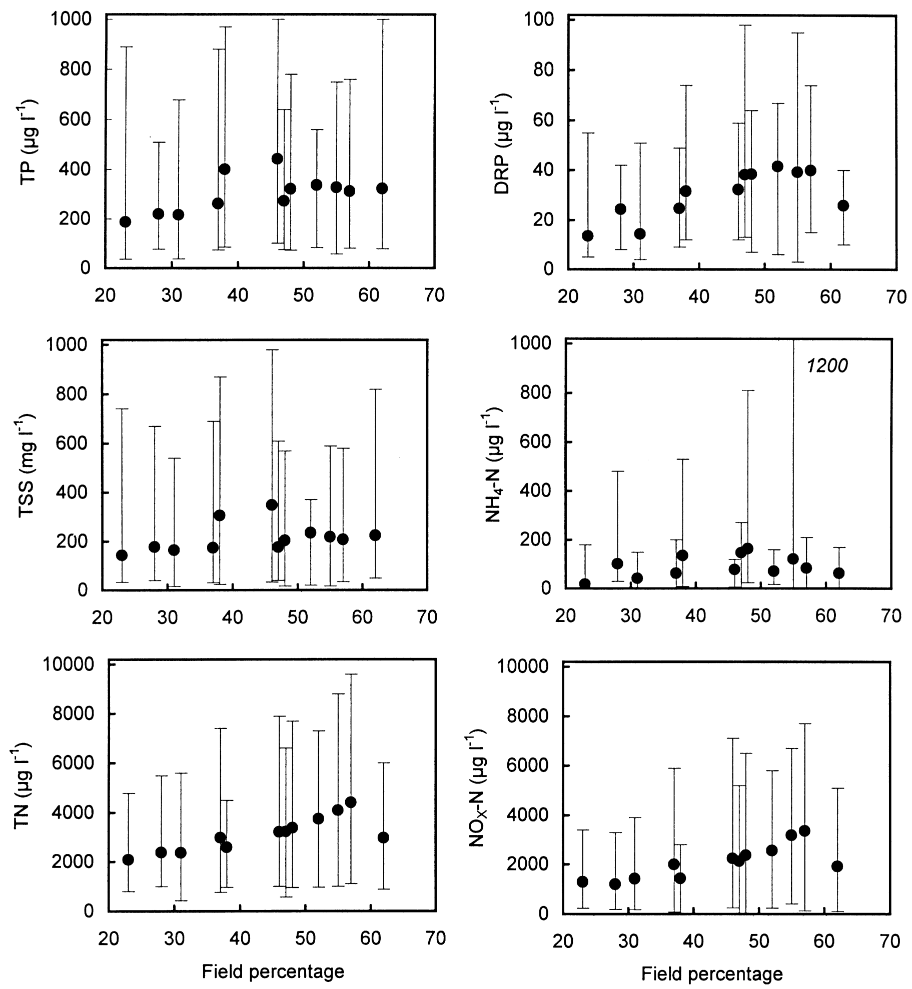

Fig. 2. Relationship between the concentrations of water quality variables and field percentage in the tributaries. Black circles denote the flow-weighted mean concentrations and bars the minimum and maximum concentrations, $n \leq 20$. TP = total P, DRP = dissolved reactive P, TSS = total suspended solids, TN = total N, NH_4-N = ammonium nitrogen, NO_x-N = the sum of nitrate and nitrite N.

The regression models best explaining the mean concentrations of TSS and TP in the tributary outlets included field percentage and the mean slope of the fields. The main-channel concentrations of TSS and TP, predicted using these regression models (see equation (2)), were in relatively good agreement with the observed concentrations (Fig. 3). With regard to TP, the predicted concentrations underestimated the observed ones by an average of 11%. In addition, the predictions could not account for the peak concentrations of TP and TSS at the site closest to the river mouth. The mean concentrations at this site were elevated by one high-flow event observation, and may thus not be entirely representative. The slight increase in the predicted TP and TSS concentrations in the lower reaches was due to steeper fields in this section.

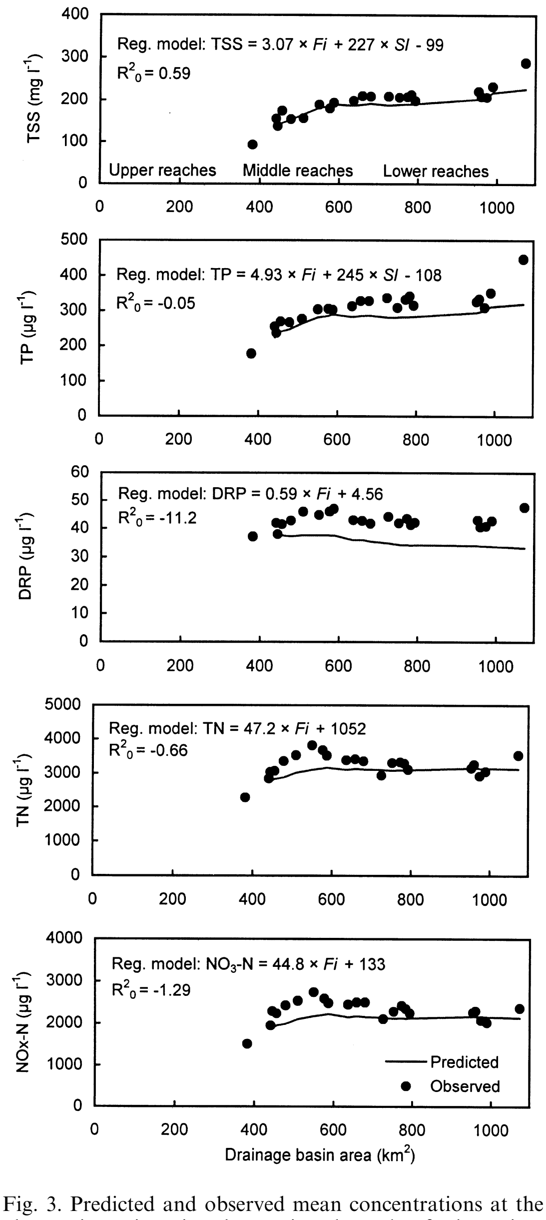

Fig. 3. Predicted and observed mean concentrations at the observation sites in the main channel of the River Paimionjoki. The predictions are based on the regression model given in each graph. *X*-axis represents the drainage basin area of each river sampling site. *Fi* = Field percentage, *Sl* = mean slope of the fields.

The observed concentrations of DRP were almost constant (43 μg l^{-1}) in the main river channel. The prediction of DRP was based on the regression model including only field percentage. The predicted concentrations decreased slowly downwards—following the distribution of fields—and were on average 17% (7.5 μg l^{-1}) too low. The observed concentrations of TN and NO_x-N were lowest at the Hovirinnankoski rapids, increased markedly in the "upper" middle reaches and were relatively constant in the lower parts of the river. The predicted concentrations of N were relatively close to the observed ones in the lower reaches, but underestimated them in the middle reaches. As in the case of DRP, the predicted TN and NO_x-N were a function of field percentage.

DISCUSSION

Effect of catchment characteristics on concentrations

In all the tributaries, fields and forests were the main sources of nutrient loading. The specific nutrient load from agricultural land is approximately 10 times the load from forested land in southern Finland (Rekolainen, 1989). Thus, it is logical that the tributary concentrations of all water quality variables, except unstable NH_4-N, increased with field percentage. The dependence of TP and TSS on the mean slope of fields is in accordance with the result, derived from field-scale measurements and modelling (e.g. Wischmeier and Smith, 1978; Rekolainen and Posch, 1991; Puustinen, 1994), that slanting fields are more prone to soil and particulate P losses than flat fields. Sharpley (1985) found that DRP concentration in surface runoff is a function of the depth of surface soil layer interacting with runoff, which on the other hand increases with slope. However, no correlation between DRP and slope was observed in the present study. The same applied for N, which is reasonable: the losses of N occur mostly as highly soluble NO_3 and are related to the reserves of organic N and their mineralisation, whereas erosion plays only a minor role in N transport.

The r^2-values for the regression models explaining DRP were smaller than those of TP and TSS. A crucial factor regulating DRP concentration is the P status of the surface soil (Yli-Halla *et al.*, 1995; Pote *et al.*, 1996). In addition, direct P losses from animal husbandry affect DRP. The municipal data indicated only negligible spatial differences in the relatively low livestock densities, whereas P status appeared to increase from the upper to the lower reaches of the River Paimionjoki. However, the applicability of municipal data is limited, because the borders of tributary catchments and municipalities did not coincide. In summary, it appears that the loss of particulate P, and TSS, on a catchment scale can be more accurately predicted with easily available catchment data than that of DRP. It is uncertain whether this is due to the lack of relevant spatial data (soil P status, texture, etc.) or of knowledge on the factors affecting the DRP loss. The same applies for N.

Riverine processes

The fraction of the total sediment eroded from a catchment that will be transported out of the basin has been observed to decrease with increasing catchment area (Walling, 1977). Prairie and Kalff (1986) found that as the catchment size increased, the delivery of TP per unit area from agricultural catchments decreased but was constant for forested basins. This discrepancy in the scale effect was suggested to be due to the difference in the form of P transported; dissolved P dominates in runoff from forested regions and particulate P in runoff from agricultural areas (Prairie and Kalff, 1986). By contrast, our results indicate no clear scale effect for TP and TSS—both variables reflecting the concentration of eroded soil matter—but suggest that DRP may increase with catchment size. First, according to the tributary data, catchment area did not explain TP or TSS, but showed a positive relationship with DRP. Second, TP and TSS at the river channel sites, which had a drainage basin area of 441–1072 km^2, were relatively accurately predicted using the regression models derived from the tributary catchments ranging from 9 to 139 km^2 in size. In contrast, the predicted DRP concentrations in the river channel were too small. In the data of Prairie and Kalff (1986), the catchments <20 km^2 were mostly responsible for the scale effect of TP. In the present study, most of the catchments were >20 km^2, which may explain the lack of scale effect for TP and TSS.

Green *et al.* (1978) found stream suspended particles to have a higher P content than the surface soils or their clay fractions in the drainage basin, and concluded that during runoff and transport suspended particles act as a sink for P. However, after deposition on the river bottom, this P may be released due to chemical and biological reactions (Green *et al.*, 1978). On the other hand, Klotz (1988) suggested that stream bottom sediments retain P from solution. Moreover, House and Warwick (1998) observed relatively large in-stream losses for dissolved P, possibly from the river water to bed sediments and suspended sediments originating from surface runoff and river bank erosion. As stated above, our results suggest release rather than retention of P in the river. Possibly, all desorbable P in eroded soil particles has not yet been released in the tributaries, but the release continues during the river transport. Judging from the mean discrepancy between the observed and predicted concentrations of DRP in the main river channel (7.5 μg l^{-1}), 2.6% of particulate P (TP–DRP) would have been released to dissolved form in the river. However, this estimate is valid only if (i) the model accurately described the DRP concentration in the runoff entering the river and (ii) the river bed sediments were inactive with regard to P. A crucial factor controlling P desorption is water–soil ratio. However, since the TSS concentrations (the reciprocal of water–soil ratio) were approximately the same in the tributary outlets and in the main river channel, water–soil ratio cannot have triggered the release of P.

CONCLUSIONS

The concentrations of TSS and TP in runoff from cropped areas increased with the mean slope of fields. This indicates that in order to decrease water turbidity and the concentrations of particulate P in river water, erosion control measures should be implemented particularly on slanting fields. However, since the availability of particulate P to algae is substantially lower than that of DRP (Ekholm, 1994), which is not affected by slope, erosion control may not effectively decrease the losses of algal-available P.

With regard to almost lakeless catchments of ca. 10–1000 km^2, the losses of TP, TSS and N per unit area appear not to depend on catchment size. By contrast, the concentration of DRP may increase with catchment area, possibly reflecting the release of P from eroded soil particles or from river bed sediments.

Since the water quality data examined here were based on a relatively infrequent sampling and there was insufficient information on the spatial differences in flow and P status and texture of surface soil, the conclusions presented can be considered only as tentative. In particular, the effects of erosion control on the losses of algal-available P require further field- and catchment-scale studies.

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