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Evaluation of Annual Loads of Nutrients and Suspended Solids in Baltic Rivers

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Estimation of pollutant fluxes through river systems calls for accurate and precise load estimation. However, considerable uncertainty is associated with these estimates due to diffuse loading, which sets high requirements not only on sampling frequencies but also on calculation methods. The aim was to examine the variation in load calculations and the reliability of the load estimates of total phosphorus, total nitrogen and suspended solids in 24 Baltic rivers varying in size and land-use characteristics. Reliability of the load estimates was tested by simulation experiments in the river Paimionjoki using a Monte Carlo procedure.

The estimates calculated by the most reliable method were compared to the loads estimated by five other methods. The general reliability (RMSE) for P and SS was best by the correlation method and for N by the periodic method. Load calculations varied greatly depending both on the characteristics of the rivers and the calculation method. The flow-stratified method overestimated the P and SS loads by about 20% in large low-lake rivers. In small low-lake rivers, the overestimation was 10% and over 14% for P and SS, respectively. By contrast, the averaging method underestimated P and SS loads by 10% and 21% in small agricultural low-lake rivers. All the methods produced rather similar results for N in each of the river types.

Introduction

Trend analyses and the assessment of sources of loading call for reliable estimates of material fluxes, which are required for allocation of resources in controlling water pollution. However, much uncertainty is involved in the estimation of material fluxes particularly in rivers receiving high diffuse pollution. This is due to the fact that the magnitude of diffuse loading depends on hydrological conditions in the watershed, which in turn sets requirements not only for the timing and frequency of water quality sampling but also for the calculation methods. Variation in load calculations is mainly due to the fact that they are based either on mean concentrations or concentrations that have been weighted by water flow in different ways. Furthermore, there are also differences in the flow-dependence of various substances.

Much effort has been made to evaluate the accuracy of load estimates for total nitrogen (N), total phosphorus (P) and suspended solids (SS) in rivers. Underestimation and lack of precision have usually been serious problems in calculating SS (Walling and Webb 1981, 1985, 1988). More reliable results for N and P have been yielded among others by ratio estimators, in which load calculations take into account the ratio between mean measured load and flow (Dolan *et al.* 1981; Richards and Holloway 1987; Preston *et al.* 1989). In one study of Nordic rivers, the most accurate and precise results for nutrients and SS were obtained by a method based on the sums of the loads at consecutive sampling intervals (Ekholm *et al.* 1995). Regression methods, taking into account the correlation between the observed concentration and water flow, have also been used successfully in estimating P load (Lathrop 1986).

In the catchment area of the Baltic Sea, several methods have been used for calculating riverine loads of nutrients (HELCOM 1994). However, only a few studies have evaluated the variation of load calculations and the reliability of the loads in Baltic rivers. These studies include evaluation of the accuracy and precision of annual nutrient loads in some Nordic rivers (Ekholm *et al.*1995) and in two agricultural basins in Finland (Rekolainen *et al.*1991). Loads based on the results from 24 monitored rivers in Finland had not been evaluated earlier. This is important because the fact that river basins have different land-use and loading characteristics is believed to affect the variation in load calculations. Furthermore, only few papers exists on the inputs of suspended solids into the Baltic Sea (*e.g.* Wartiovaara 1978; Lajczak and Jansson 1993).

The aim of this study was to examine the variation in load calculations and the reliability of the annual loads of P, N and SS in different types of Finnish rivers. The reliability of the load was tested by using simulation by a Monte Carlo procedure, which was earlier applied by *e.g.* Richards and Holloway (1987), Rekolainen *et al.* (1991), and deVries and Klavers (1994). The loads produced by the most reliable method were compared to those estimated by five other methods.

Material and Methods

Rivers

The studied 24 rivers cover 87% of the Finnish catchment area. The river basins were highly variable in their morphometric and land-use characteristics (Fig. 1,

Table 1). The surface area of the basins varied between 566 and 51,127 km^2, the mean water flow during the study period ranging from 6 to 397 m^3 s^{-1}. Six of the river basins were larger than 14,000 km^2. The percentage of watershed under agriculture varied between 0.5 and 44%. The river basins were defined as agricultural when the field percentage exceeded 10%. In other cases the basins were forested. The lake percentage varied between 0.2 and 17%. The division between low and high lake percentage of a basin was set at 5%.

In order to examine the effects of different kinds of river basins on the load estimates, the rivers were divided into five classes according to the main characteristics of the basins : 1) large rivers with low lake percentage, 2) large rivers with high lake percentage 3) small agricultural rivers with low lake percentage, 4) small agricultural rivers with high lake percentage, and 5) small forested rivers with low lake percentage (Table 2).

The characteristics of the watersheds are reflected in the hydrological conditions. Due to the high lake percentage and the large drainage area in the large rivers, the seasonal variations of water flow are usually smaller and the average residence times of water much longer than in small coastal rivers. On the other hand, in small coastal rivers the seasonal variations of water flow and water quality are usually great because hydrological conditions (such as snow melting) are immediately reflected in water flows. Moreover, there is a strong dependence between field-percentage and nutrient fluxes in river catchments with lake percentage below 5% (Pitkänen 1994).

Chemical Analyses

The water quality and water flow data of 24 rivers discharging into the Baltic Sea during 1986-1995 originated from the national environmental data base of Finland (Fig.1, Table 1). Total nitrogen (N) samples were oxidized with potassium peroxodisulphate and reduced to NO_2-N in Hg-Cd or Cu-Cd columns and determined colorimetrically. Total phosphorus (P) samples were digested by $K_2S_2O_8$ to reactive form and then analysed spectrophotometrically by the ammonium molybdate method of Murphy and Riley (1962) with ascorbic acid as a reducing agent. In the case of suspended solids (SS), samples were filtered through a glass fibre filter (< 70 g/m^2, GF/C), dried at 105°C, and then determined gravimetrically. The frequency of the water quality samples varied in general from 10 to 20 per year. Water flow was measured daily.

Monte Carlo Method

The accuracy and precision for load estimates of the five calculation methods were evaluated by applying the Monte Carlo procedure earlier used *e.g.* by Richards and Holloway (1987) and Rekolainen *et al.* (1991). Daily data sets for P, N and SS were formed by linear interpolation from the weekly monitored water quality data of the river Paimionjoki for the years 1985 and 1988-91 in order to include variation of

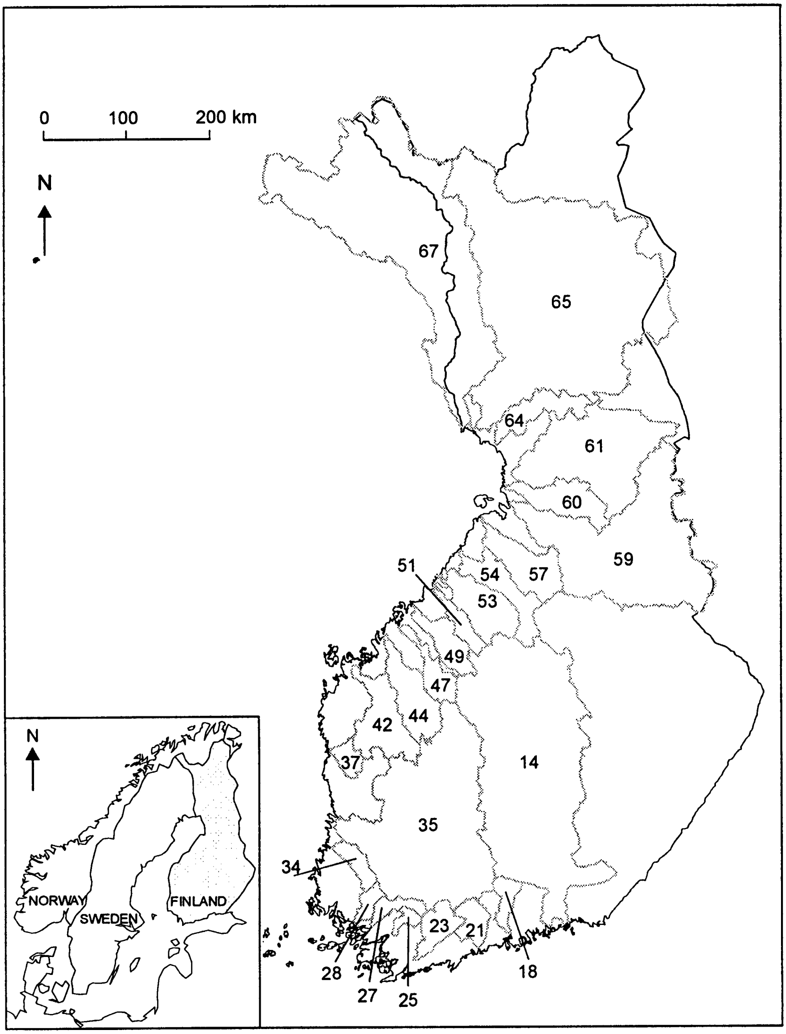

Fig. 1. Rivers discharging from Finland into the Baltic Sea.

daily water flow in the calculation. The flow-dependent strategy of 12 annual samples included one sample per month in January to March, six samples per month in April to May, one sample per month in June to August, three samples per month in September to October and one sample per month in November to December. By using this strategy, one hundred replicate data sets were randomly sampled from the daily data set for each substance.

The replicate data sets for each method were used to calculate the accuracy and precision of the load estimates. Accuracy, *i.e.* the deviation from the reference ("true") value was computed as

Table 1 – Main characteristics of the studied rivers, their drainage basins and mean flows in 1986-1995. Drainage areas of the rivers, field percentages and lake percentages of the river basins originate from the Environment Data Base of the Finnish environment Institute.

Catchment/ River basin	drainage area, km^2	lake area %	field area %	mean flow m^3 s^{-1} 1986-95
14, Kymijoki	37159	17.3	24.6	349.5
18, Porvoonjoki	1273	1.3	28.5	13.9
21, Vantaa	1686	2.3	23.4	16.6
23, Karjaajoki	2046	12.2	29.9	20.7
25, Uskelanjoki	566	0.6	43.7	6.4
27, Paimionjoki	1088	1.5	43.0	10.3
28, Aurajoki	877	0.3	36.7	8.6
34, Eurajoki	1336	12.8	29.1	10.4
35, Kokemäenjoki	27046	10.0	27.0	271.7
37, Isojoki	1098	0.2	11.5	14.9
42, Kyrönjoki	4923	1.2	23.4	45.6
44, Lapuanjoki	4122	2.7	20.8	39.1
47, Ähtävänjoki	2054	9.9	13.3	16.5
49, Perhonjoki	2524	3.0	9.5	23.0
51, Lestijoki	1373	5.9	12.1	12.9
53, Kalajoki	4247	1.9	14.9	41.2
54, Pyhäjoki	3712	5.0	9.4	34.0
57, Siikajoki	4318	2.2	7.1	43.4
59, Oulujoki	22841	11.7	5.0	263.2
60, Kiiminkijoki	3814	3.2	2.0	43.5
61, Iijoki	14191	5.8	1.1	167.7
64, Simojoki	3160	5.7	1.2	40.9
65, Kermijoki	51127	4.1	0.7	568.7
67, Tornionjoki	35000	4.7	0.5	420.0

Table 2 – Criteria for the river classes.

River class	drainage area, km^2	lake %	field %	n
Large poor-lake rivers	> 14000	< 5	< 2	3
Large rich-lake rivers	> 14000	> 5	5-27	3
Small agricultural poor-lake rivers	< 5000	< 5	> 10	9
Small agricultural rich-lake rivers	< 5000	> 5	> 10	4
Small forested poor-lake rivers	< 5000	< 5	< 10	5

$$\text{accuracy} = 100\,\frac{L_{\text{est}}-L_{\text{ref}}}{L_{\text{ref}}}\,\% \qquad (1)$$

where L_{ref} is the annual reference value calculated from the daily data set and L_{est} is the mean value of the load computed from one hundred replicate data sets.

Precision, *i.e.* the scatter around the mean value, was computed as the coefficient of variation of the loads computed from the replicate data sets.

$$\text{precision} = 100\,\frac{S_{\text{est}}}{L_{\text{est}}}\,\% \qquad (2)$$

where S_{est} is the standard deviation of the one hundred replicate estimates of loads.

It is, however, difficult to obtain a good result for accuracy and precision simultaneously. If one method has good accuracy, its precision is weak and *vice versa* (*e.g.* Walling and Webb 1981; Rekolainen *et al.* 1991). In order to describe the general reliability of the studied methods, the root mean squared error (RMSE, Bickel and Doksum 1977) was calculated as

$$RMSE = \sqrt{\text{accuracy}^2+\text{precision}^2} \qquad (3)$$

Load Calculations

Annual loads were estimated by six methods: averaging, linear interpolation, periodic, correlation, partially flow-stratified and flow-stratified methods, of which the second last is a new method. The method giving the most accurate and precise loads was chosen as the comparison method, of which the absolute loads were presented. The results by the other methods were given as percentages of the load calculated by the comparison method.

Method 1 (Averaging method)

The annual river loads (L_a) were calculated by multiplying the mean monthly concentration by the mean monthly flow and summing up the monthly loads

$$L_a = \sum_{m=1}^{12} c_m q_m \qquad (4)$$

where c_m is the observed instantaneous concentration in month m (mean in the case of several samples per month or seasonal average in the case of missing monthly observations) and q_m is the mean monthly flow calculated from the daily flow values.

Method 2 (Linear interpolation method)

In Method 2, daily concentration between two observations was estimated linearly. The very first observation in the data set was used for determining the concentrations of the preceding days and the last for the concentrations of the postceding days. The annual river loads (L_a) were calculated by summing up the daily loads

$$L_a = \sum_{d=1}^{365^*} c_d q_d \qquad (5)$$

where c_d is the observed concentration or the daily concentration between two successive observations determined linearly and q_d is the measured daily water flow.

Method 3 (Periodic method)

The annual river loads (L_a) were calculated by summing up the loads in the sampling interval

$$L_a = \sum_{i=1}^{n} c(t_i)\, q(T_i) \qquad (6)$$

where $c(t_i)$ is the concentration on day t_i obtained from the interpolated data set and $q(T_i)$ is the water flow for the sampling interval T_i (the period between the midpoints of sampling occasions). The number of sampling intervals (n) is also the number of samples taken.

Method 4 (Correlation method)

The positive correlation between the concentration (c) and the measured daily water flow (q) enabled use of the correlation method for P and SS (Table 3). With regard to N, the corresponding correlation was weak. In order to calculate concentrations for lacking days the parameters a and b were first determined by means of the smallest sum of squares

$$\log(c) = a + b \log(q) \qquad (7)$$

Because of the rather infrequent concentration data and the usual failures in observing the events of high water flows, a period of five years was used for determining the parameters a and b. On an annual basis, the correlation often remained unclear. The use of log transformation aimed at decreasing the unreliability of the parameters a and b, which resulted from the skewness of the data (Table 3). Log transformation is commonly used for skewed data sets and for data including strong seasonal variation (see Smith and Stewart 1977; Ferguson 1986). The concentrations of lacking days (c_{est}) were calculated as

$$c_{est} = 10^a q^b \qquad (8)$$

The correction factor CF for the bias originating from the log transformations was derived according to Ferguson (1986) as

Table 3 – Coefficient of correlation between log-transformed water flow and concentration, and skewness of the concentrations of P, N and SS in 1985-1995.

River	coefficient of correlation			skewness		
	P	N	SS	P	N	SS
Large low-lake rivers						
Iijoki	0.62*	0.19*	0.68*	1.31	0.70	3.14
Kemijoki	0.67*	0.26*	0.67*	1.96	1.40	4.25
Tornionjoki	0.27	0.03	0.53*	2.21	1.45	3.58
mean	**0.52***	**0.16***	**0.63***	**1.83**	**1.18**	**3.66**
Large rich-lake rivers						
Kymijoki	0.02	0.03	0.04*	1.34	1.05	2.43
Kokemäenjoki	0.17*	0.16*	0.18*	2.52	2.20	2.66
Oulujoki	-0.02	-0.02	0.01	2.48	1.45	3.93
mean	**0.06**	**0.06**	**0.08***	**2.11**	**1.57**	**3.00**
Small agricultural low-lake rivers						
Porvoonjoki	0.31*	-0.30*	0.76*	1.31	1.90	1.86
Vantaa	0.43*	0.01	0.61*	2.05	1.03	1.85
Uskelanjoki	0.38*	0.18*	0.45*	1.64	1.42	2.42
Paimionjoki	0.28*	0.16*	0.18*	1.68	1.35	2.19
Aurajoki	0.38*	0.13*	0.46*	2.54	3.91	3.72
Isojoki	0.11*	0.37*	0.56*	3.19	0.83	3.82
Kyrönjoki	0.06*	0.12*	0.75*	1.73	1.98	2.42
Lapuanjoki	0.05*	0.06*	0.57*	2.81	2.27	3.78
Kalajoki	0.27*	0.11*	0.44*	3.27	1.20	4.07
mean	**0.25**	**0.09***	**0.53***	**2.25**	**1.77**	**2.90**
Small agricultural rich-lake rivers						
Karjaanjoki	-0.00	0.04*	0.08*	3.44	2.27	7.03
Eurajoki	0.21*	0.04*	0.54*	3.24	1.34	2.41
Ähtävänjoki	0.04*	0.11*	0.20*	6.04	0.72	4.77
Lestijoki	0.16*	0.13*	0.57*	3.74	1.71	4.40
mean	**0.10**	**0.08***	**0.35***	**4.12**	**1.51**	**4.65**
Small forested low-lake rivers						
Perhonjoki	0.03*	0.04*	0.22*	3.59	2.32	9.62
Pyhäjoki	0.42*	0.16*	0.77*	1.65	1.17	1.62
Siikajoki	0.12*	0.20*	0.58*	2.83	1.39	5.45
Kiiminkijoki	0.06*	-0.02	0.38*	2.16	3.11	2.63
Simojoki	0.57*	0.25*	0.61*	5.98	1.92	7.95
mean	**0.24***	**0.13***	**0.51***	**3.24**	**1.98**	**5.45**

*) Levels of significance ($0.01<p_{obs}<0.05$)

$$CF = \exp(2.651\, S^2) \tag{9}$$

where

$$S^2 = \sum_{i=1}^{n} (\log c_i - \log c_{i(\mathrm{est})})^2 (n-2)^{-1} \tag{10}$$

where c_i is the concentration of observation i, $c_{i(est)}$ is the concentration for the same observation derived from the regression *e.g.* Eq.(8) using the water flow of the observation day, and n is the number of observations. The annual load was estimated as the sum of daily loads as

$$L_a = \sum_{d=1}^{365^*} c_d\, q_d\, CF \tag{11}$$

where c_d is observed or estimated concentration and q_d is daily flow.

Method 5 (Partially flow-stratified method)

In developing Method 5, the features of Methods 1, 4 and 6 were applied in order to improve the accuracy of the load estimates. It was attempted to avoid underestimating of the load by using flow-weighting (see Method 6) for high flow periods. Flow-weighted mean concentrations were calculated by using data from high flow periods of five years. This was done for the same reason as in Method 4, *i.e.* because the observations representing high flow periods were often missing. Overestimation was purposed to be avoided by using unweighted, arithmetic mean concentrations for the periods of low water flow. Non-weighted mean concentrations were calculated in the same way as in Method 1, on a monthly, seasonal or annual basis. The division between high and low flow was drawn on the basis of visual inspections of flow diagrams at 25% of the annual maximum flow. The annual load was calculated as

$$L_a = \sum_{i=1}^{365^*} c_d\, q_d. \tag{12}$$

where the values of c_d are observed concentrations or estimated flow-stratified mean concentrations for the high-flow days or estimated unstratified mean concentrations for low-flow days, and q_d is observed daily water flow.

Method 6 (Flow-stratified method)

In Method 6, flow-weighted mean concentration was calculated for each year by dividing the annual mean products of observed concentrations and water flows by annual mean water flows $q(t_i)$ of the sampling days. The annual load was calculated by multiplying flow-weighted mean concentration and annual mean water flow q_a

$$L_a = q_a \frac{\frac{1}{n}\sum_{i=1}^{n} c(t_i)\, q(t_i)}{\frac{1}{n}\sum_{i=1}^{n} q(t_i)} \tag{13}$$

where $c(t_i)$ is the observed daily concentration, $q(t_i)$ the observed daily water flow, q_a the mean annual water flow and n the number of observations.

Results

Accuracy and Precision of Load Estimates

On the basis of the Monte Carlo simulation experiments of the river Paimionjoki, which had most frequent (weekly) monitoring data, Methods 4 (correlation method) and 5 (partially flow-stratified method) usually produced the most accurate results for the loads of P (about -3% bias), whereas clearly the best precision (about 5% scatter) was obtained by Method 4 (Table 4). On the basis of RMSE, the general reliability of the loads of P was best with Method 4.

The most accurate results for the load of N were obtained by Methods 3 (periodic method), with the bias of -5%. The reason for great over- and underestimations by Methods 4 and 5 was the fact that these methods were based on the data of the five-year period, during which the mean annual concentrations of N varied considerably. The best precision (5% scatter) was obtained with Method 4. On the basis of RMSE, the general reliability of the load of N was best with Method 3.

The estimates of SS were unbiased in Methods 4 and 6, with an underestimation on average of less than 6%. In some years, however, both high over- and underestimates were obtained. Method 4 produced the best precision, with a scatter of less than 10% for each year. On the basis of RMSE, the general reliability of the load of SS was best with Method 4.

Variation in Load Calculations

The annual load estimates varied considerably depending both on the method and the type of the river basin (Table 5). On the basis of the results of the general reliability (RMSE), the loads of P were mainly underestimated by Methods 1-3 (averaging method, linear interpolation method and period method) and overestimated by Methods 5-6 (partially flow-stratified method and flow-stratified method). Overestimation was greatest in large rivers with low lake percentage, where Method 6 produced on average 18% greater loads than Method 4 (correlation method). The loads were also about 10% greater in small rivers. By contrast, Method 1 gave about 10% lesser loads than Method 4 in small agricultural rivers with low lake percentage.

In the case of N, the loads were usually underestimated by Methods 1-2 and overestimated by Methods 4-6. Nevertheless, the load calculations did not differ from

Table 4 - Accuracy, precision and RMSE for the load estimates of total phosphorus, total nitrogen and suspended solids in the River Paimionjoki in 1985 and 1988-1991.

Method/Criteria	Phosphorus						Nitrogen						Suspended solids					
	1985	1988	1989	1990	1991	**mean**	1985	1988	1989	1990	1991	**mean**	1985	1988	1989	1990	1991	**mean**
Method 1																		
Accuracy	-15.4	-12.4	-11.1	-14.8	-10.6	**-12.9**	-12.7	-5.6	-8	2.8	-6.9	**-6.1**	-29.5	-11.3	-6.4	-15.4	-24.2	-17.4
Precision	11	13.5	20.9	34.2	14.1	**18.7**	10.2	8.7	19.6	17.4	10	**13.2**	18.5	17	37.5	48.6	25.7	29.5
MRSE	18.9	18.3	23.7	37.3	17.6	**23.2**	16.3	10.3	21.2	17.6	12.1	**15.3**	34.8	20.4	38	51	35.3	35.9
Method 3																		
Accuracy	-8.5	-9.5	-9.9	-15.9	-9.9	**-10.7**	-5	-4.4	-8	-1.2	-6.6	**-5**	-12.8	-11.3	-11.1	-18.7	-13.4	-13.5
Precision	11	10.3	21.8	32.6	12.7	**17.7**	9.6	8.4	18.3	15.3	9	**12.1**	20.8	13.5	36.6	43.5	23.4	27.6
MRSE	13.9	14	23.9	36.3	16.1	**20.8**	10.8	9.5	18	15.3	11.1	**12.9**	24.4	17.6	38.2	47.3	27	30.9
Method 4																		
Accuracy	-7.6	-5.6	11.7	-16.1	0.1	**-3.5**	26.8	20.2	-14.2	-21.1	-11.7	**0**	12.8	-1.8	-0.1	-16.1	-21.9	-5.4
Precision	5	5.3	5	6	5.6	**5.4**	5.6	4.9	5.2	5.4	5.1	**5.2**	7	7.4	8.5	9.1	7.9	8
MRSE	9.1	7.7	12.7	17.2	5.6	**10.5**	27.4	20.8	15.1	21.8	12.8	**19.5**	14.5	8.2	8.5	18.5	23.3	14.6
Method 5																		
Accuracy	-6.2	-1.1	10.4	-15.9	-0.2	**-2.6**	-1.2	4.4	-14.2	-26.6	-12	**-9.9**	-10.7	1.6	5.6	-25.5	-13.8	-8.6
Precision	9.4	12.3	10.1	15	9.5	**11.3**	7.3	7.5	7.7	9.4	7.6	**7.9**	16.7	16.7	15	13.4	14.7	15.3
MRSE	11.3	12.3	14.5	21.9	9.5	**13.9**	7.4	8.6	16.1	28.2	14.2	**14.9**	19.8	16.8	16	28.8	20.2	20.3
Method 6																		
Accuracy	5.5	5	-9.4	-14.3	-6.5	**-3.9**	-0.4	1.2	-18.2	-4.9	-4.4	**-5.3**	14.3	14.8	-13	-15.6	-14.5	-2.8
Precision	19.9	17.7	11.1	23.6	15.7	**17.6**	7.9	12.2	15.4	12	9	**11.3**	31.4	27.3	22.3	29	23.9	26.8
MRSE	20.6	18.4	14.5	27.6	17	**19.6**	7.9	12.3	23.8	13	10	**13.4**	34.5	31.1	25.8	32.9	28	30.5

Table 5 – The loads of P and SS (t/a) by Method 4 (correlation method) and the loads of N (t/a) by Method 3 (periodic method), and differences of the loads of P, N and SS (%) estimated by the other methods compared to those given by Method 4 (for P and SS) and by Method 3 (for N).

	P						N						SS					
River type/Meth	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6
Large low-lake rivers																		
Lijoki	-5	-3	-2	142	1	16	0	0	2126	0	2	5	-11	-7	0	21577	3	-1
Kemi	-4	-3	-3	446	4	21	1	0	6614	1	1	7	-8	1	-2	74191	15	36
Tornio	-9	-11	-10	366	4	17	-14	-18	4019	-10	-12	-6	-15	-10	-12	81453	9	29
mean	**-6.0**	**-5.7**	**-5.0**	**317**	**3.0**	**18.0**	**-4.3**	**-6.0**	**4245**	**-3.0**	**-3.0**	**2.0**	**-11.3**	**-5.0**	**-4.7**	**58840**	**9.0**	**21.3**
Large rich-lake rivers																		
Kymi	-2	-2	-2	293	1	2	0	0	7055	1	1	2	-8	-8	-8	61774	-4	-6
Kokoem	-3	-1	-1	487	3	4	0	-1	9959	3	3	3	-3	-1	-1	119559	3	5
Oulu	-9	-10	-10	182	1	0	1	0	3010	6	5	6	-18	-22	-22	40877	3	1
mean	**-4.7**	**-4.3**	**-4.3**	**329**	**1.7**	**2.0**	**0.3**	**-0.3**	**6377**	**3.3**	**3.0**	**3.7**	**-9.7**	**-10.3**	**-10.3**	**73488**	**0.7**	**0.0**
Small agricultural low-lake rivers																		
Porvoo	-7	-6	-6	62	5	12	2	3	1469	-1	3	-8	-21	-18	-15	17604	3	23
Vantaa	-10	-9	-9	69	6	13	5	4	1320	9	3	3	-23	-24	-21	31346	5	13
Usk	-21	-17	-15	53	6	4	0	0	499	15	4	8	-36	-34	-30	29524	-2	-5
Paim	-10	-7	-6	81	2	2	-1	-1	905	10	7	2	-19	-20	-19	39405	4	2
Aura	-14	-5	-4	57	10	11	-8	-3	750	9	7	4	-20	-12	-9	27153	16	14
Iso	-2	-2	0	35	18	17	-3	-2	527	1	3	3	-16	-7	-2	7990	27	30
Kyrön	-6	-2	-1	160	9	11	-2	-1	3226	0	4	3	-15	-6	-3	46605	17	18
Lapuan	-6	-7	-6	135	7	9	0	-1	2214	-2	3	6	-7	-7	-5	26113	23	26
Kala	-11	-9	-9	182	0	8	0	-1	1921	6	3	6	-30	-24	-22	37441	-4	5
mean	**-9.7**	**-7.1**	**-6.2**	**93**	**7.0**	**9.7**	**-0.8**	**-0.2**	**1478**	**5.2**	**4.3**	**2.9**	**-20.8**	**-16.9**	**-14.0**	**29434**	**9.9**	**14.0**
Small agricultural rich-lake rivers																		
Karjaan	4	4	4	24	4	4	0	0	656	-2	-2	-1	10	9	10	4284	20	18
Eura	-9	-1	1	23	17	14	0	-1	632	-2	6	5	-12	-9	-7	10737	16	10
Ähtävän	-15	-15	-15	25	2	-5	0	0	421	8	6	2	-5	-5	-4	4839	7	2
Lesti	9	7	6	43	15	22	2	1	460	0	1	6	-4	13	14	8196	28	42
mean	**-2.8**	**-1.3**	**-1.0**	**29**	**9.5**	**8.8**	**0.5**	**0.0**	**546**	**1.0**	**2.8**	**3.0**	**-2.8**	**2.0**	**3.3**	**7052**	**17.8**	**18.0**
Small forested low-lake rivers																		
Perhon	2	0	0	66	7	12	3	1	755	4	3	6	-13	-8	-7	8487	2	9
Pyhä	-14	-11	-11	74	-6	8	-2	-1	1080	2	1	6	-31	-21	-19	15605	-8	15
Siika	-5	-4	-3	133	2	10	-1	0	1544	1	3	7	-19	-8	-6	30583	8	20
Kiim	0	-1	-1	51	0	9	2	1	735	0	0	1	-6	0	0	9076	3	26
Simo	0	3	4	37	13	25	-1	0	668	-2	1	5	13	20	23	6811	36	52
mean	**-3.4**	**-2.6**	**-2.2**	**70**	**3.2**	**12.8**	**0.2**	**0.2**	**938**	**1.0**	**1.6**	**5.0**	**-11.2**	**-3.4**	**-1.8**	**13553**	**8.2**	**24.4**

each other more than 5% in any of the types of river basins. However, in a few small agricultural rivers with low lake percentage (the rivers Vantaa, Uskelanjoki, Paimionjoki, Aurajoki) the loads were about 10% greater than those obtained by Method 3, whereas in the river Porvoonjoki Method 6 exceptionally produced 8% smaller loads.

The pattern of the load calculations of SS resembled that of P although the under- and overestimations were greater. In large rivers with low lake percentage, Method 6 produced 21% greater loads than Method 4, but the loads were also 14 to 24% greater in all small agricultural and forested rivers, respectively. By contrast, Methods 1-3 gave 14 to 20% smaller loads than Method 4 in small agricultural low-lake rivers.

Discussion

Application of a Monte Carlo Procedure to the River Paimionjoki

The application of the Monte Carlo method requires frequent data sets, *e.g.* daily observation or at least observations frequent enough to be able to generate a reference data by interpolation or extrapolation. The smaller the watershed and the greater the variations in the short-duration events of water flows, the more frequent should the reference data be. In addition, with particulate-associated substances the demand on the number of observations is greater than with substances transported in solution (Richards and Holloway 1987; Ekholm *et al.* 1995).

In this study, daily observations were not available from any of the rivers. The river Paimionjoki was the best test river for small agricultural rivers. However, its application as a reference for large rivers did not weaken the results, because the variation of concentrations in studied rivers was greatest in small agricultural rivers. The daily data sets were generated from the weekly data of the river Paimionjoki by linear interpolation and the replicate data sets. The error caused by the use of a small number of observations in the interpolation was compensated by the analysis of several years of data.

Evaluation of Calculation Methods

On the basis of RMSE, the most reliable results for P and SS were obtained with Method 4, which depends on correlation between concentration and water flow. Method 3, which takes into account the direction of the slope of water flow independently of water volume in estimating the lacking concentrations, produced the best results for N. This is in accordance with the study by Arheimer *et al.* (1996), who found that significant correlation between flow and the concentration of N in small forested streams could be either positive or negative, and that in general only 20% of the variation of N concentration could be explained by variation in flow volume.

This indicated that other factors than flow volume must be considered for accurate load estimates.

In the load calculations of P, accuracy and precision using Method 4 remained below 10% on the periodic basis of five years. However, in some years the loads were over- or underestimated by more than this amount but precision was always good. Reasonably accurate load estimates for P have also been gained by other regression methods (cf.Young *et al.* 1988) and even more accurate results by Beale ratio estimator (*e.g.* Dolan *et al.* 1981), presumably due to the lower sensitivity of the method to differences in tributary characteristics (Lathrop 1986; Preston *et al.* 1989).We did not use this method because it appears to require a greater number of samples than the correlation method in order to achieve the same level of precision (Preston *et al.* 1989).

The load estimates of SS were precise and on a periodic basis accurate. However, bias up to 20% was observed in some individual years. Underestimation was more common than overestimation. Only by increasing sampling numbers many fold has it been possible by Methods 1, 3 and 6 to obtain unbiased results (Ekholm *et al.* 1995). However, in some small agricultural rivers, even the use of weekly data together with a correction factor was not sufficient to yield accurate loads for SS, probably due to error associated with rating curves (Walling and Webb 1988). Furthermore, the degree of the underestimation appeared to increase with decreasing basin size.

Factors affecting accuracy of the loads of particulate-associated substances may also include lack of coincidence of concentration and discharge responses during snow-melting or storm events (Walling and Webb 1988); the phenomenon reported among other also by Sharpley *et al.* 1976 and Ulén (1995). In our data, the concentration peaks of P and SS did not match the peak of water flow in the beginning of the snow-melt period, which can be explained by the considerable seasonal variation in erosivity (Posch and Rekolainen 1993). During the time when soil is frozen and the surface runoff fraction is high, desorption rather than erosion is responsible for high losses of P (Rekolainen 1989b). According to Lathrop (1986), season was the only significant stratification factor for dissolved P, whereas event intensity was the most important for particulate P.

Contrary to P and SS, the load estimates of N obtained by Method 3 were accurate, and on a periodic basis precise. This method has also been used successfully by Walling and Webb (1981), Rekolainen *et al.* (1991) and Ekholm *et al.* (1995). As all the methods yielded rather similar load estimates for N, the choice of the method is less important than in the cases of P and SS.

Reasons for Variation in Load Calculations

The applicability of a calculation method to a substance and to the characteristics of a river basin brought variability to the load estimation. Overestimations for the loads of P and SS were most considerable by Method 6 (flow-stratified method) especial-

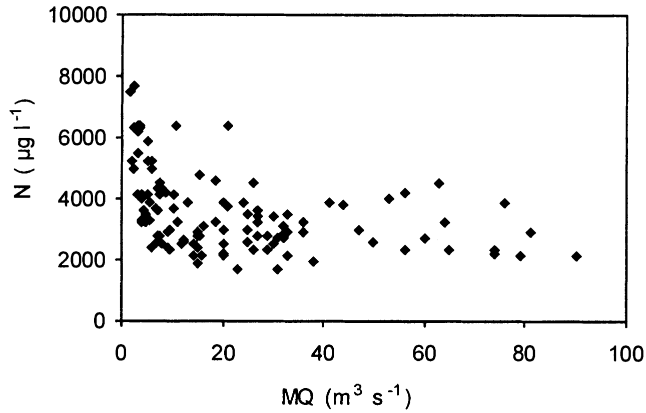

Fig. 2. The relationship of load of total nitrogen (N, ug l^{-1}) and mean annual water flow (m^3 s^{-1}) in the river Porvoonjoki during 1986-1995.

ly in large low-lake rivers but also in small low-lake rivers (Table 5). The benefit of Method 4 (correlation method) in calculating the loads in low-lake rivers was caused by high correlation between concentration and water flow (Table 3) due to low retention. Nutrients are not permanently retained in large low-lake rivers such as the river Kemijoki (Kauppila unpubl. data) nor in small agricultural rivers (Rekolainen *et al.* 1995). Under- or overestimations remain relatively small only in large rivers with high lake percentage, where the retention of substances are considerable.

In the case of N, the load calculations did not differ much from the loads estimated by Method 3 (periodic method) in any of the river types. This was mainly due to the low correlation between concentrations and water flow, because N is transported mainly in solution. As an exception to this pattern, however, in some individual rivers the load calculations of N differed by about 10% from those obtained by Method 3 (Table 5). A clearly smaller load estimates (such as in river Porvoonjoki) was explained by substantial municipal input of N compared to total fluxes. This was also exhibited as the negative correlation between concentration and water flow mainly due to dilution of point source effluent (Fig. 2). According to Johnson (1979) and Preston *et al.* (1989), constituents that are non-reactive *(e.g.* major ions) may be controlled by dilution which is indicated by an exponentially decreasing relationship. Additionally, Pitkänen (1994) and Rekolainen *et al.* (1995) found that N transport did not correlate with field percentage in this river. Some other small agricultural rivers characterized by high losses of N (Kauppi 1979; Rekolainen 1989a) yielded about 10% greater load estimates compared to Method 3 (Table 5).

Summary and Conclusions

On the basis of Monte Carlo simulations, the general reliability (RMSE) for P and SS was best by Method 4 (correlation method) and for N by Method 3 (periodic method). The annual loads of P and SS were precise, whereas accurate loads were obtained only for a five-year period. In the case of N, the situation was opposite: the loads were precise on a periodic basis and accurate on an annual basis. Consequently, with the present monitoring schemes the use of a correlation method is justified for the trend analysis of P and SS only on a periodic basis.

The load calculations of P and SS varied greatly depending on the method and the characteristics of the river basin. The flow-stratified method overestimated the P and SS loads by about 20% in large rivers with low lake percentage. In small agricultural and forested rivers with low lake percentage, the overestimation by this method was about 10% for P and 14 to 24% for SS, respectively. By the averaging method, P and SS loads were underestimated most (10% and 21% respectively) in small agricultural rivers with low lake percentage. In the case of N, all the methods produced rather similar results in each of the river types.

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