



# Development, validation and application of Danish empirical phosphorus models

H.E. Andersen\*, B. Kronvang, S.E. Larsen

*National Environmental Research Institute, Department of Freshwater Ecology, Vejlsoevej 25, DK-8600 Silkeborg, Denmark*

Received 30 November 2003; revised 1 May 2004; accepted 1 July 2004

## Abstract

Phosphorus (P) is the limiting nutrient for algae growth in most Danish lakes and coastal waters. Discharge of P from point sources has been reduced greatly, however, no trend in diffuse P loss has been detected. In spite of the overall reduction in P discharge, the ecological condition of most lakes and coastal waters does not comply with the objectives set by regional authorities. Thus, in order to achieve ‘good ecological status’ of surface waters, as required by the EU Water Framework Directive, there is a future need to reduce diffuse P loss. Consequently, water district managers will need tools for assessing diffuse P losses at the catchment scale. They will also need tools to help them select for each specific catchment the appropriate measures to reduce P losses. We suggest that empirical phosphorus models can be an important part of such a tool. A number of international empirical phosphorus models are reviewed. The development, validation and application of six Danish empirical phosphorus models for total phosphorus (TP), particulate phosphorus (PP) and dissolved reactive phosphorus (DRP) is described as a case study. Manageable parameters relating to agricultural practices are generally absent in the international models reviewed. In the Danish models such parameters play a relatively minor role compared to non-manageable parameters like soil type and hydrology. The importance of validating empirical models and of uncertainty assessments on model predictions is stressed.

© 2004 Elsevier B.V. All rights reserved.

*Keywords:* Phosphorus; Diffuse losses; Empirical models; Validation; Uncertainty assessment

## 1. Introduction

Phosphorus (P) is the limiting nutrient for algae growth in most Danish lakes and coastal waters (Kronvang et al., 1993). Despite the achievement in many European countries of large reductions in P

discharges from point sources, the water quality of rivers, lakes and estuaries nevertheless continues to deteriorate due to diffuse P losses (Sharpley et al., 2000; Kronvang et al., 2002). In Denmark, discharge of P from point sources has been reduced greatly, by 86% since 1989, however, no trend in diffuse P loss has been detected. Diffuse P loss thus constitutes an increasing part and now makes up more than 50% of total P-loss from agricultural areas to surface waters (Kronvang et al., this volume). Although net input of

\* Corresponding author. Tel.: +45 89201400; fax: +45 89201414.

E-mail address: [hea@dmu.dk](mailto:hea@dmu.dk) (H.E. Andersen).

P to agricultural land has decreased from 14.8 to 8.8 kg ha<sup>-1</sup> during 1989–2001 (Grant et al., 2002) the P status of cultivated land, and thus the risk of P loss via leaching and erosion, is increasing. The soils highest in P status are found in areas with high livestock numbers and thus concentrated in certain regions of Denmark. In spite of the overall reduction in P discharge, the ecological condition of most lakes and coastal waters does not comply with the objectives set by regional authorities (Jensen et al., 2002). Thus, in order to achieve 'good ecological status' of surface waters, as required by the EU Water Framework Directive, there is a need to reduce diffuse P losses. Consequently, water district managers will need tools for assessing diffuse P losses at the catchment scale. They will also need tools to help them select for each specific catchment the appropriate measures to reduce P losses (Heathwaite et al., 2000). Mechanistic, dynamic models do fulfil these requirements (e.g. Schoumans and Groenendijk, 2000), however, the input data necessary to set up mechanistic models are seldom available. Besides, setting up and running mechanistic models requires expert skills and is very time consuming. Therefore the primary use of such models will be in scenario analysis on the few catchments with existing high-quality data sets. Empirical models, on the other hand, require considerably less input data, expert skills and time for setting up and running. We suggest that empirical catchment models developed on or calibrated against regional data sets can be a valuable tool for water district managers in complying with the Water Framework Directive. In this paper we present a review of existing empirical P models. In order to demonstrate how to develop, validate and apply empirical models we present as a case study a set of recently developed Danish empirical P models.

## 2. Materials and methods

### 2.1. Catchment data

A large Danish data set comprising detailed information from 24 agricultural catchments on physiography, land use and farming practises at the field level was used for developing empirical P models (Table 1). Regarding inputs of P to the soil,

data on P in organic fertilisers was used rather than data on total fertiliser-P. The reason for this is, that in Denmark input of P in surplus of plant demand is exclusively connected to application of organic fertilisers (Grant et al., 2002). The geographic distribution of the catchments (Fig. 1) ensures that the climatic gradient as well as regional differences in soil types and farming practices are covered. The catchments are predominantly under arable cultivation.

### 2.2. Measurements

Water stage was recorded in the stream at the outlet of all catchments every 10 min by automatic stage recorders. Discharge was measured monthly. A stage–discharge relationship was used to construct time series of daily discharge. Quick flow (i.e. the fastest responding part of the stream flow hydrograph) and Base Flow Index (i.e. the proportion of baseflow of total flow) was calculated for all catchments by the method of Institute of Hydrology (1993). Water samples were collected with automatic samplers at all catchment outlets using either a time or a flow proportional sampling strategy. Prior to analysis, water samples were pooled to give weekly means. Additionally, a point sample was collected every week at all stations. The composite water samples were analysed for total P (TP), whereas point samples were analysed for dissolved reactive P (DRP). Weekly TP transport was calculated by summing the products of pooled weekly concentration and weekly discharge. Annual TP transport was subsequently calculated by summing weekly transports. Daily DRP concentrations were obtained by linear interpolation between sampling dates and annual DRP transport then calculated by summing the products of daily discharge and estimated daily DRP concentration (Kronvang and Bruhn, 1996). It has been shown for small catchments (Kronvang and Bruhn, 1996) that estimates of DRP transport based on point samples underestimate the 'true' transport of DRP by only ca. 7%. Transport of TP and DRP are thus considered to be estimated by the same degree of accuracy, and hence particulate P (PP) is calculated as TP–DRP. Discharge-weighted concentration of all three P fractions was calculated by dividing annual transport with annual discharge. Sampling started in

Table 1  
Characteristics of the 24 catchments

Station	County	Area (km <sup>2</sup> )	Sand (%)	Loamy subsoil (%)	Arable land (%)	P applied (org. fert. kg P ha <sup>-1</sup> )	Point sources (kg P ha <sup>-1</sup> )	Runoff (mm yr <sup>-1</sup> )	Base flow index	PP (%)	TP transport (kg P ha <sup>-1</sup> )
130011	Nordjylland	11.4	89	0	83	20.6	0	289	0.80	69	0.52
160030	Viborg	11.3	62	100	82	20.7	0	222	0.58	83	0.77
210072	Aarhus	3.9	17	100	86	19.7	0	185	0.60	85	0.23
210752	Aarhus	5.5	21	92	68	16.0	0.004	277	0.69	53	0.27
210759	Aarhus	10.6	18	94	81	25.5	0.012	252	0.66	58	0.32
210803	Viborg	10.6	6	82	83	15.0	0	271	0.56	60	0.32
210872	Vejle	22.0	17	91	84	26.5	0	359	0.64	68	0.74
220043	Ringkøbing	19.0	26	78	81	20.2	0.002	303	0.45	75	0.94
350011	Ribe	6.6	99	0	77	15.2	0	492	0.83	65	0.55
360012	Ribe	9.5	36	71	84	14.9	0.017	510	0.86	62	0.70
360030	Vejle	3.7	23	72	85	12.0	0	360	0.68	43	0.35
380020	Vejl/Sjyl	10.8	30	94	81	20.6	0.042	425	0.67	68	0.46
420012	Sønderjylland	7.8	86	21	85	22.2	0.005	482	0.86	86	0.41
470001	Fyn	57.8	33	72	65	9.8	0.040	296	0.75	48	0.32
470033	Fyn	4.4	0	100	85	31.7	0	252	0.61	41	0.45
480011	Frederiksborg	8.9	90	13	65	0.8	0.001	93	0.70	66	0.17
520033	Frederiksborg	5.4	78	31	86	6.3	0.002	104	0.78	76	0.25
520199	Roskilde/Kbh	27.0	26	94	76	1.2	0.112	122	0.55	84	0.21
570044	Vestsjælland	15.2	13	100	75	5.5	0.091	209	0.58	43	0.22
570063	Vestsjælland	12.3	16	99	75	11.8	0	226	0.79	71	0.43
580019	Vestsj/Rosk	4.3	27	100	48	3.1	0	180	0.51	63	0.16
620014	Storstrøm	9.9	12	95	60	2.9	0	120	0.75	66	0.15
620022	Storstrøm	15.4	0	100	71	5.7	0.006	171	0.61	62	0.20
660014	Bornholm	41.9	28	n.d.	79	17.7	0.008	188	0.69	45	0.19

Data shown are for 2000. Sand: percentage of the topsoils identified as sandy. Loamy subsoils: percentage of subsoils identified as loamy. Arable land: percentage of total catchment area. P applied in org. fert.: P applied in manure and slurry as average for the total catchment area. Point sources: Contribution of P from point sources in the catchment. Runoff: Discharge measured at the catchment outlet divided by catchment area.. Base Flow Index: proportion of baseflow of total flow. Calculated by the method of Institute of Hydrology (1993). PP: diffuse transport of PP in percent of diffuse TP transport. TP transport: annual catchment diffuse loss of TP. n.d.: no data.

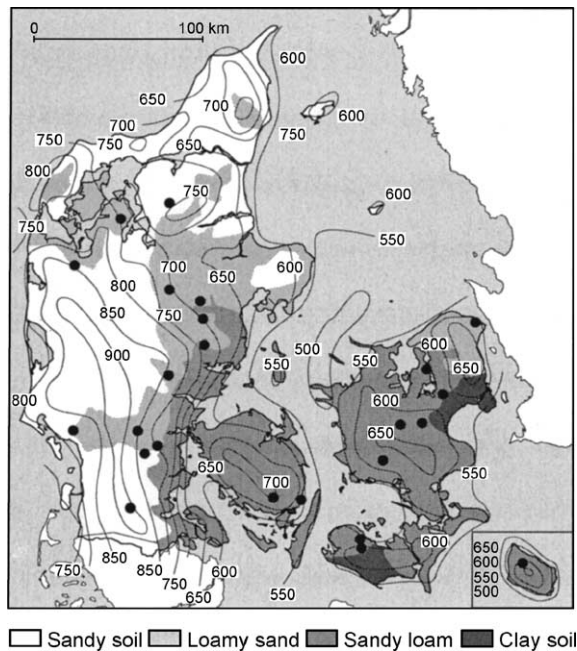


Fig. 1. Location of the 24 Danish catchments (black dots), dominant soil types and average annual precipitation in Denmark.

most catchments in 1994 and data are available up to 2002. The data set thus includes measurements for 1996 that had an extremely low precipitation (505 mm), and 1999 that had the highest precipitation measured since systematic measurements started in 1874 (905 mm). The huge range in precipitation strengthens the data set as a basis for developing empirical models. Point source contribution of TP was measured 2–24 times annually at all sewage treatment plants receiving inputs from more than 30 person equivalents (PE). Point source contribution of TP from smaller sewage treatment plants and individual households was estimated based on information on the number of PE's and wastewater treatment type, and assuming that the annual discharge from one PE equals 1 kg TP (Miljøstyrelsen, 1999).

### 2.3. Statistical methods

The relationships between three fractions of either annual P transport or annual discharge-weighted P concentration and a set of explanatory variables were estimated by the use of multiple regression analysis (Rawlings, 1988). Before estimating the models,

intercorrelations were investigated by Spearman Rank Correlation (Snedecor and Cochran, 1989). From groups of strongly intercorrelated variables, only one variable was selected for further testing in the multiple regression analyses. The set of explanatory variables was reduced sequentially to only the ones significant at a 5% level of significance. Standard errors of parameters in the final model can be used to calculate standard errors on model predictions (Rawlings, 1988).

## 3. Results and discussion

### 3.1. Review of empirical P models

Since Dillon and Kirchner (1975) made their review on P export for different categories of geology and land use types in catchments, several attempts have been made to relate P export to climate, geology, land use, etc. within the catchment (Table 2). A common feature of the empirical models shown in Table 2 is that the majority have been developed on a rather coarse catchment scale (10–100 km<sup>2</sup>). Another common feature is that the models nearly always incorporate an explanatory variable related to agricultural pressure, often as the proportion of agricultural land in the catchment. Very few of the models include explanatory variables that relate directly to agricultural practices, such as application of P in animal manure, chemical fertiliser, or crop types. Simulation of the effects of catchment management strategies with empirical P models will require that this type of explanatory variable is included in the models. Most of the hitherto developed empirical models can, therefore, only be applied for simulation of very rigid management strategies (e.g. reduction in proportion of agricultural land) or be applied for simulation of P export from unmonitored catchments to surface water bodies.

An empirical approach to P loss modelling different from the regression models shown in Table 2 is the export coefficient model approach, e.g. Johnes (1996). Export coefficient modelling is an upscaling approach where the export coefficients for individual nutrient sources are derived from literature sources or field experiments. An export coefficient model needs to be calibrated against observed water

Table 2

Overview of empirical models of annual P export ( $T$ , units: kg P ha<sup>-1</sup>) or annual P concentration (C) as functions of different explanatory variables at the catchment level

Country/area	Empirical model	Reference
East Texas, USA	$T_{\text{TP04}} = 18.121(P)^{0.57} (\text{Comp})^{-1.74}$	Chang et al. (1983)
California—Nevada, USA	$C_{\text{TP}} = 12 + 933.3(\text{HD})$	Byron and Goldman (1989)
Finland	$T_{\text{TP}} = 0.95 + 0.014\text{AL}$	Rekolainen (1989)
Central Pomerania, Poland	$\log(T_{\text{PP}}) = 0.35 \log(\text{AL}) - 1.14$	Taylor et al. (1986)
Noteć region, Poland	$\log(T_{\text{TP}}) = 3.59 \log(\text{AL}) - 7.55$	Taylor et al. (1986)
River Rönneå, Sweden	$T_{\text{TP}} = 0.12 + 0.0083\text{AL}$	Diehl et al. (1987)
Estonia <sup>a</sup>	$T_{\text{TP}} = 0.025 \text{AL} + 0.12$	Loigu (1991)
Denmark	$\ln(T_{\text{TP}}) = a + 1.09 \ln(R) + 1.2\text{AL} - 0.26S$	Kronvang et al. (1995)
Latvia <sup>a</sup>	$T_{\text{TP}} = 1.76 + 11.85 \log(\text{AL} + 1)$	Loigu (1989)
Denmark	$T_{\text{TP}} = -0.0019(S) + 0.00605(O) + 0.000648(R) + 0.01164(P)$	Kronvang et al. (2003)
Norway	$T_{\text{TP}} = -0.45 + 0.07(S_{\text{AL}}) + 0.001(\text{SS}) + 0.13(O)$	Kronvang et al. (2003)
European micro-catchments	$\ln(T_{\text{TP}}) = -2.96 + 0.0156(\text{AL}) + 0.0024(R) + 0.0145(\text{CA})$	Kronvang et al. (2003)
River Basin Finland <sup>b</sup>	$C_{\text{TP}} = 3.49\text{AL} + 149$	Ekholm et al. (2000)

TP, total phosphorus; PP, particulate phosphorus; DRP, dissolved reactive phosphorus; AL, proportion of agricultural land (%);  $R$ , annual runoff (mm);  $S$ , percentage of sandy soils (%);  $O$ , percentage of organic soils (%);  $P$ , average application of phosphorus with manure and fertiliser in the catchment (kg P/ha);  $S_{\text{AL}}$ , average soil P content (mg/100 g soil); SS, export of suspended sediment (kg/ha); CA, catchment area (km<sup>2</sup>);  $P$ , percentage of pasture (%); comp, watershed compaction (watershed perimeter/watershed area multiplied with 0.282); HD, proportion of high disturbance areas (%).

<sup>a</sup> Unit in kg P km<sup>-2</sup>.

<sup>b</sup> Unit  $\mu\text{g P l}^{-1}$ .

quality data before application, whereas regression models can be used directly. Regression models should, however, be restricted in use to the range of land use, climate, soil type and P management for which they were developed and application of such models in other regions/countries will always demand a careful verification, validation and testing (Heathwaite, 2002).

### 3.2. Developing empirical models on the Danish data set

Point source contributions were subtracted from the transport estimates assuming a ratio of dissolved P to particulate bound P in point source contributions of 1:4 (Karin Laursen, personal communication). Hereby also the discharge-weighted concentrations are corrected for point sources. Data up to 2000 were used for developing empirical models. Six models were developed describing the relationships between parameters characterising the catchment and either transport or concentration of TP, PP and DRP. Tables 3–8 present the six developed models for transport and concentration of TP, PP and DRP. For each model the overall coefficient of determination

Table 3  
Model for transport of TP

Overall coefficient of determination, $R^2$	0.80	$p < 0.0001$
Parameter	Coefficient of determination, $R^2$	Estimate
Intercept		-6.53289
$\ln(\text{Quick flow})$	0.65	0.86483
AL	0.06	0.01865
$S$	0.06	0.00629
Slope	0.02	0.01405
Buffer	0.01	-0.03833
Correction for skewness	1.06	

Quick flow, the fastest responding part of the stream flow hydrograph, determined by the method of Institute of Hydrology (1993); AL, percentage of arable land;  $S$ , percentage of sandy topsoils; slope, slope of stream bed; buffer, percentage of riparian meadow and wetland; Runoff, runoff in mm yr<sup>-1</sup>; P in organic fertilizer, P applied in manure or slurry on average for fields receiving manure or slurry, in kg P ha<sup>-1</sup>; P from scattered dwellings, P contribution from scattered dwellings not connected to a sewer system in kg P ha<sup>-1</sup>; BFI, Base Flow Index, i.e. the proportion of base flow of total flow determined by the method of Institute of Hydrology (1993).

Table 4  
Model for transport of PP

Overall coefficient of determination, $R^2$	0.75	$p < 0.0001$
Parameters	Coefficient of determination, $R^2$	Estimate
Intercept		-7.66341
ln(Quick flow)	0.56	0.92078
S	0.10	0.00917
AL	0.08	0.02295
Buffer	0.005	-0.04124
Slope	0.004	0.01869
Correction for skewness	1.09	

Quick flow, the fastest responding part of the stream flow hydrograph, determined by the method of [Institute of Hydrology \(1993\)](#); AL, percentage of arable land; S, percentage of sandy topsoils; slope, slope of stream bed; buffer, percentage of riparian meadow and wetland; Runoff, runoff in  $\text{mm yr}^{-1}$ ; P in organic fertilizer, P applied in manure or slurry on average for fields receiving manure or slurre, in  $\text{kg P ha}^{-1}$ ; P from scattered dwellings, P contribution from scattered dwellings not connected to a sewer system in  $\text{kg P ha}^{-1}$ ; BFI, Base Flow Index, i.e. the proportion of base flow of total flow determined by the method of [Institute of Hydrology \(1993\)](#).

Table 5  
Model for transport of DRP

Overall coefficient of determination, $R^2$	0.65	$p < 0.0001$
Parameters	Coefficient of determination, $R^2$	Estimate
Intercept		-6.96884
ln(Runoff)	0.54	0.86286
Buffer	0.05	-0.09313
P in organic fertilizer	0.03	0.01136
P from scattered dwellings	0.03	1.37733
Correction for skewness	1.11	

Quick flow, the fastest responding part of the stream flow hydrograph, determined by the method of [Institute of Hydrology \(1993\)](#); AL, percentage of arable land; S, percentage of sandy topsoils; slope, slope of stream bed; buffer, percentage of riparian meadow and wetland; Runoff, runoff in  $\text{mm yr}^{-1}$ ; P in organic fertilizer, P applied in manure or slurry on average for fields receiving manure or slurre, in  $\text{kg P ha}^{-1}$ ; P from scattered dwellings, P contribution from scattered dwellings not connected to a sewer system in  $\text{kg P ha}^{-1}$ ; BFI, Base Flow Index, i.e. the proportion of base flow of total flow determined by the method of [Institute of Hydrology \(1993\)](#).

Table 6  
Model for concentration of TP

Overall coefficient of determination, $R^2$	0.39	$p < 0.0001$
Parameters	Coefficient of determination, $R^2$	Estimate
Intercept		-2.21518
Baseflow index	0.13	-1.62123
AL	0.11	0.01550
S	0.10	0.00519
Buffer	0.04	-0.06679
Slope	0.01	0.01838
Correction for skewness	1.06	

Quick flow, the fastest responding part of the stream flow hydrograph, determined by the method of [Institute of Hydrology \(1993\)](#); AL, percentage of arable land; S, percentage of sandy topsoils; slope, slope of stream bed; buffer, percentage of riparian meadow and wetland; Runoff, runoff in  $\text{mm yr}^{-1}$ ; P in organic fertilizer, P applied in manure or slurry on average for fields receiving manure or slurre, in  $\text{kg P ha}^{-1}$ ; P from scattered dwellings, P contribution from scattered dwellings not connected to a sewer system in  $\text{kg P ha}^{-1}$ ; BFI, Base Flow Index, i.e. the proportion of base flow of total flow determined by the method of [Institute of Hydrology \(1993\)](#).

Table 7  
Model for concentration of PP

Overall coefficient of determination, $R^2$	0.39	$p < 0.0001$
Parameters	Coefficient of determination, $R^2$	Estimate
Intercept		-2.77435
S	0.19	0.00862
AL	0.10	0.01856
BFI	0.07	-2.13255
Slope	0.02	0.02181
Buffer	0.005	-0.04992
Correction for skewness	1.10	

Quick flow, the fastest responding part of the stream flow hydrograph, determined by the method of [Institute of Hydrology \(1993\)](#); AL, percentage of arable land; S, percentage of sandy topsoils; slope, slope of stream bed; buffer, percentage of riparian meadow and wetland; Runoff, runoff in  $\text{mm yr}^{-1}$ ; P in organic fertilizer, P applied in manure or slurry on average for fields receiving manure or slurre, in  $\text{kg P ha}^{-1}$ ; P from scattered dwellings, P contribution from scattered dwellings not connected to a sewer system in  $\text{kg P ha}^{-1}$ ; BFI, Base Flow Index, i.e. the proportion of base flow of total flow determined by the method of [Institute of Hydrology \(1993\)](#).

Table 8  
Model for concentration of DRP

Overall coefficient of determination, $R^2$	0.29	$p < 0.0001$
Parameters	Coefficient of determination, $R^2$	Estimate
Intercept		−2.35977
BFI	0.16	−1.06651
Buffer	0.10	−0.08761
P in organic fertilizer	0.04	0.01097
Correction for skewness	1.11	

Quick flow, the fastest responding part of the stream flow hydrograph, determined by the method of Institute of Hydrology (1993); AL, percentage of arable land; S, percentage of sandy topsoils; slope, slope of stream bed; buffer, percentage of riparian meadow and wetland; Runoff, runoff in  $\text{mm yr}^{-1}$ ; P in organic fertilizer, P applied in manure or slurry on average for fields receiving manure or slurry, in  $\text{kg P ha}^{-1}$ ; P from scattered dwellings, P contribution from scattered dwellings not connected to a sewer system in  $\text{kg P ha}^{-1}$ ; BFI, Base Flow Index, i.e. the proportion of base flow of total flow determined by the method of Institute of Hydrology (1993).

( $R^2$ ) is shown together with the contribution to the overall  $R^2$  of each individual parameter. Runoff, quick flow, P transport, and P concentration have entered the regression analyses in a logarithmic form (natural logarithm). This was done to ensure a normal distribution of the residuals, since it was assumed, and subsequently controlled, that raw data were log-normally distributed. In order to re-instate this skewness when using the models for calculating estimates of P transport or P concentration, the estimates should be multiplied with a factor (Ferguson, 1986). This factor for correction for skewness is given for each model in Tables 3–8. The estimated empirical models are linear and additive for the log-transformed response variables (P concentration and P transport). This means that in the original measured scale the empirical models are on a multiplicative form.

The overall coefficient of determination is high for the transport models. This is partly due to the fact that stream flow is part of the transport calculation and used as an explanatory variable. In the models for transport of TP and PP it is, however, only a fraction of total flow (namely the quick flow) that is used for modelling. In Denmark, quick flow is mainly associated with flow from drainage pipes and shallow

groundwater, whereas surface runoff contributes only a few millimetres on an annual basis. This indicates that flow from the root zone, via tile drains and shallow groundwater, is an important transport route for P from arable land to surface water in Danish catchments (Kronvang et al., 2002). The relatively poorer coefficients of determination for the concentration models illustrate the difficulties in modelling the complicated relationships between source and transport factors and the spatial and temporal variation herein (Gburek et al., 2000). The models might be improved by increasing the temporal resolution to, e.g. monthly values. Hereby, some of the within-year fluctuations in discharge and the temporary retention in the stream bed could be taken into account. On the other hand, the models would be more complicated both to construct and to use. It is generally the same explanatory variables in the transport and concentration models. Discharge or quick flow is substituted in the concentration models by the Base Flow Index, which enters all models negatively. This means that P concentration decreases with increasing proportion of deeper groundwater flow, again highlighting the importance of drain pipes and shallow groundwater as contributors of P to surface water.

Observations of rill erosion on fields sloping towards the stream were available for all 24 catchments, but did not contribute significantly to the models. The reason is most likely that erosion in Danish catchments is of only minor importance for total P export, and thus is difficult to model (Kronvang et al., 2000; Laubel et al., 2000). Stream bank erosion is generally assumed to make up a relatively large part of total P export from Danish catchments (Laubel et al., 2003). Observations of stream bank failure were available for all catchments, but did not contribute significantly to the models. However, bank failure can be caused by various phenomena; undercutting by stream water, trampling down by cattle, or by traffic of heavy machinery close to the stream (Lawler, 1992). Bank failure is thus of a very stochastic nature and consequently difficult to model. For all models, the manageable parameters (extent of arable land, application of P in organic fertiliser, buffer between arable land and stream) contribute relatively little to the overall coefficient of determination.

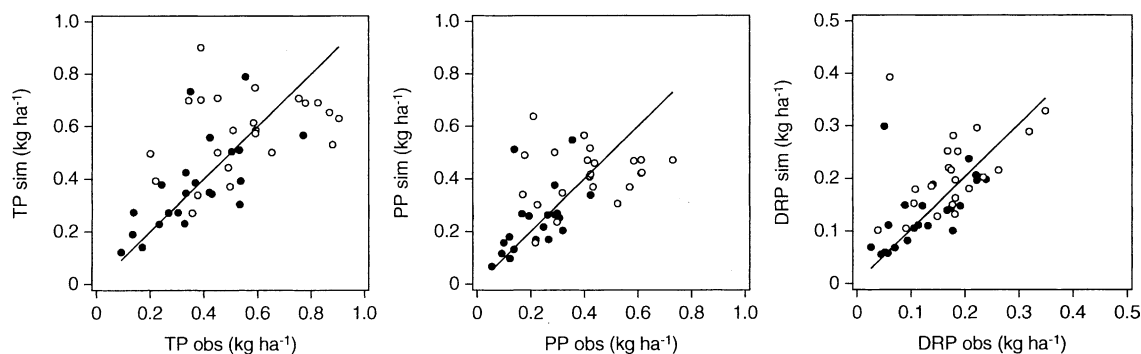


Fig. 2. Comparison of observed (obs) and simulated (sim) values of transport of TP, PP, and DRP. Dots: 2001; circles: 2002. As an illustration of model uncertainty a 95% confidence interval is calculated for one predicted value located in the centre of the distribution of predicted values, for each value: TP:  $0.5 \text{ kg P ha}^{-1}$  with a 95% confidence interval  $[0.43\text{--}0.58] \text{ kg P ha}^{-1}$ . PP:  $0.4 \text{ kg P ha}^{-1}$  with a 95% confidence interval  $[0.34\text{--}0.47] \text{ kg P ha}^{-1}$ . DRP:  $0.2 \text{ kg P ha}^{-1}$  with a 95% confidence interval  $[0.17\text{--}0.24] \text{ kg P ha}^{-1}$ .

### 3.3. Validating empirical models

The models were developed on data up to 2000. Data for 2001 and 2002 thus form independent data sets on which the models were validated. Figs. 2 and 3 show a comparison of simulated and observed values for the transport and concentration models, respectively. The transport values (Fig. 2) are distributed symmetrically around the line of identity, with the largest scatter for the 2002 data. This is due to the fact that runoff in 2002 was extremely high and thus at the borderline of the range of validity where model uncertainty is the largest. The model for transport of DRP yields the best description of the independent data sets, except for two outliers. This is a catchment

with very large runoff in 2001 and 2002 and thus very large predicted values. The measured values of DRP are, however, very small due to a high concentration of iron in the stream water (ca.  $2 \text{ mg total-Fe l}^{-1}$ ). The high iron content causes precipitation of DRP and PP thus makes up 88% of TP in this stream. The lower coefficients of determination of the concentration models result in a larger asymmetry of the values around the line of identity. This again illustrates the need for further improvement of the models. Data on soil P status and P binding capacity were not available for the catchments, but should be included in future modelling attempts. As an illustration of the uncertainty on the model predictions, 95% confidence limits have been calculated for one predicted value

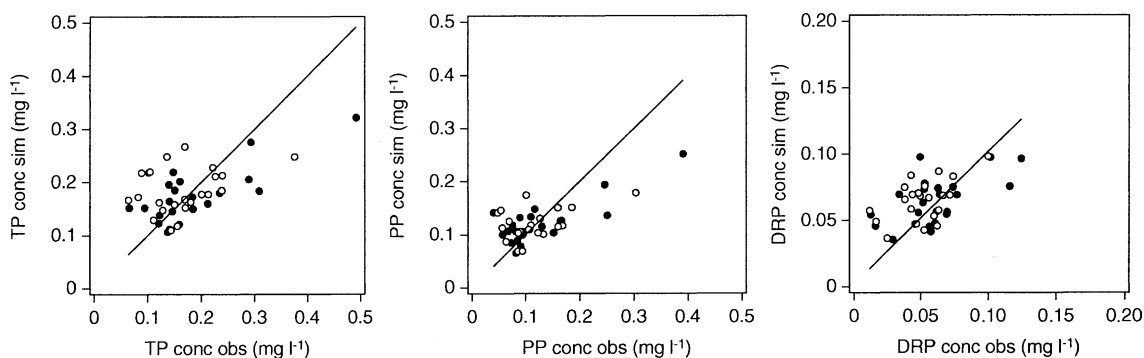


Fig. 3. Comparison of observed (obs) and simulated (sim) values of concentration of TP, PP, and DRP. Dots: 2001; circles: 2002. As an illustration of model uncertainty a 95% confidence interval is calculated for one predicted value located in the centre of the distribution of predicted values, for each model: TP:  $0.150 \text{ mg P l}^{-1}$  with a 95% confidence interval  $[0.132\text{--}0.171] \text{ mg P l}^{-1}$ . PP:  $0.100 \text{ mg P l}^{-1}$  with a 95% confidence interval  $[0.088\text{--}0.115] \text{ mg P l}^{-1}$ . DRP:  $0.050 \text{ mg P l}^{-1}$  with a 95% confidence interval  $[0.038\text{--}0.066] \text{ mg P l}^{-1}$ .



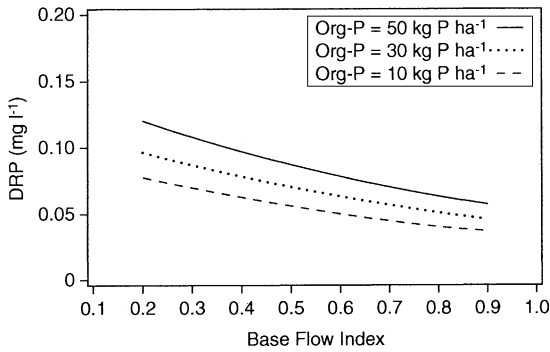


Fig. 4. Calculations with the model for concentration of DRP for three levels of application of P in organic fertiliser (Org-P).

located in the centre of the distribution of predicted values, for each value (Figs. 2 and 3). Since each point in the figures represents one catchment for 1 year, and therefore an individual combination of explanatory variables it is not possible to construct, e.g. a common 95% confidence band around the line of identity.

3.4. Applying empirical models

Fig. 4 shows an example on prognostic use of empirical models: concentration of DRP has been calculated as a function of Base Flow Index for three levels of P applied in organic fertiliser. The concentration of DRP increases with increasing P application, and decreases with increasing value of the Base Flow Index. Fig. 5 illustrates the same model calculations, only now it is 95%-confidence bands around the predicted values that are shown. From Fig. 5 it is evident that all confidence bands overlap.

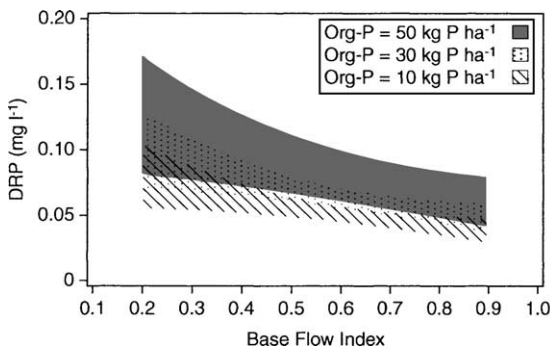


Fig. 5. Calculations with the model for concentration of DRP for three levels of application of P in organic fertiliser (Org-P). 95%-confidence bands are shown.

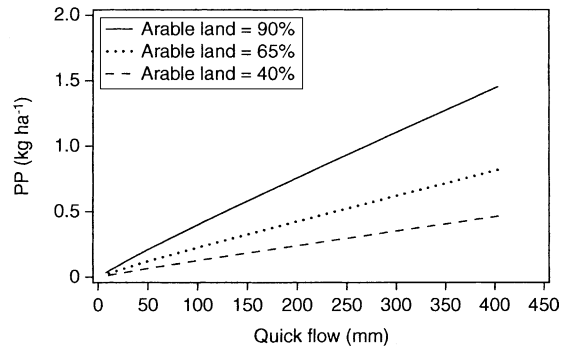


Fig. 6. Calculations with the model for transport of PP for three levels of extent of arable land.

The consequence is that it is not possible with statistical significance (5% level) to separate predicted values for the three levels of applied P in organic fertiliser. Predictions of the effect on concentration of DRP, of a change in application of P in organic fertiliser, is thus without meaning at least for the 10–50 kg P ha⁻¹ range in P application shown here. Another example of model predictions is shown in Fig. 6. The model for transport of PP has been used to predict transport values as a function of quick flow for three levels of extent of arable land. The same model predictions are shown in Fig. 7 but now as 95%-confidence bands. From Fig. 7 it is seen that the effect of 90% arable land is significantly different (5%-level) from the effects of both 65 and 40% arable land. However, the effects of 65% arable land and 40% arable land can only be separated up to a quick flow value of ca. 200 mm. Table 9 shows the effect of a reduction in extent of arable land from 90 to 40%

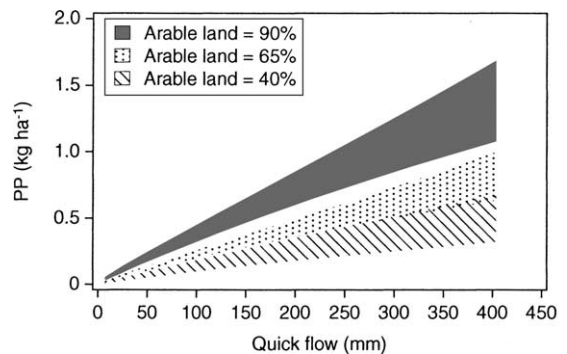


Fig. 7. Calculations with the model for transport of PP for three levels of extent of arable land. 95%-confidence bands are shown.

Table 9  
Calculation of transport of PP for two levels of quick flow

Quick flow (mm)	Arable land (%)	PP transport (kg P ha <sup>-1</sup> )	Lower 95%-confidence limit (kg P ha <sup>-1</sup> )	Upper 95%-confidence limit (kg P ha <sup>-1</sup> )
80	90	0.32	0.27	0.37
80	40	0.11	0.08	0.15

in a catchment with a quick flow of 80 mm, typical of a loamy Danish catchment. Transport of PP will be lowered almost two-thirds from 0.32 to 0.11 kg P ha<sup>-1</sup> by this rather drastic measure.

Transfer of these P models developed on a Danish data set to other countries is not a straightforward case. A definite requirement before application of the models is a test of model validity on a local data set. In many cases the models are bound to fail because factors, that influence on P loss but which are not included in the models as explanatory variables, are different from country to country. For example, application of manure and slurry on frozen soil is not practised in Denmark, whereas it might be a common feature in other countries. Such a difference in application practise will result in a very different availability of P for loss via snow melt. Moreover, differences in topography, soils and climate between countries mean that different hydrological pathways are responsible for the transport of P from land to surface water. For example in Norway, P loss is strongly associated to snowmelt causing erosion and surface runoff (Kronvang et al., 2003), whereas in Denmark, P loss via tile drains and upper groundwater is a more important transport route for P losses (Kronvang et al., 2002).

#### 4. Conclusions

Six empirical models on annual transport and annual discharge-weighted concentration of TP, PP and DRP were developed on a Danish data set of a high standard. Overall, coefficients of determination for the transport models were high (0.65–0.80), but relatively poor for the concentration models (0.29–0.39). A large number of easy to use empirical P models is available, however, because the models are empirical it is important to obey the range of validity of each particular model. A model should

therefore be developed on or calibrated against data from the region where it is intended for use. Equally important is validation of the model on an independent data set. Evaluation of uncertainty on model predictions should always be performed, in order to test whether model statements are statistically significant and thus meaningful. The model review and the Danish P models show that manageable parameters generally play a small role in the overall determination. This might be due to a lack of such data in the model data sets, however this was not the case for the Danish models.

#### Acknowledgements

This work was supported by the Danish Natural Research Programme (CONWOY; SNF No. 2052-01-0034).

#### References

- Byron, E.R., Goldman, C.R., 1989. Land-use and water quality in tributary streams of Lake Tahoe, California-Nevada. *J. Environ. Qual.* 18, 84–88.
- Chang, M., McCullough, J.D., Granillo, A.B., 1983. Effects of land use and topography on some water quality variables in forested east Texas. *Water Resour. Bull.* 19 (2), 191–196.
- Diehl, S., Enell, M., Leonardson, L., 1987. Eutrophication of the Bay of Skälderviken—a Study of Nutrient Loading and Nutrient Sources in the River Rönneå Drainage Basin 1978–1984. *Vatten* 43, 13–25.
- Dillon, P.J., Kirchner, W.B., 1975. The effects of geology and land use on the export of phosphorus from watersheds. *Water Res.* 9, 135–148.
- Ekholm, P., Kallio, K., Salo, S., Pietilainen, O.-P., Rekolainen, S., Laine, Y., Joukola, M., 2000. Relationship between catchment characteristics and nutrient concentrations in an agricultural river system. *Water Res.* 34 (15), 3709–3716.
- Ferguson, R.I., 1986. River loads underestimated by rating curves. *Water Resour. Res.* 22, 74–76.
- Gburek, W.J., Sharpley, A.N., Heathwaite, L., Folmar, G.J., 2000. Phosphorus management at the watershed scale: a modification of the Phosphorus index. *J. Environ. Qual.* 29, 130–144.

- Grant, R., Blicher–Mathiesen, G., Andersen, H.E., Jensen, P.G., Pedersen, M., Rasmussen, P., 2002. Landovervågningsoplande 2001. NOVA 2003. Danmarks Miljøundersøgelser. Faglig rapport fra DMU nr. 420 (in Danish).
- Heathwaite, L., 2002. Empirical phosphorus export models, 35–41, in: Kronvang, B. (Ed.), Diffuse Phosphorus Losses at Catchment Scale. COST Action 832. Alterra, Wageningen, The Netherlands.
- Heathwaite, L., Sharpley, A., Gburek, W., 2000. A conceptual approach for integrating phosphorus and nitrogen management at the watershed scales. *J. Environ. Qual.* 29, 158–166.
- Institute of Hydrology, 1993. Low flow estimation in the United Kingdom. IH Report No. 108. Institute of Hydrology, Wallingford, UK.
- Jensen, J.P., Søndergaard, M., Bjerring, R., 2002. Søer 2001. NOVA 2003. Danmarks Miljøundersøgelser. Faglig rapport fra DMU 421 (in Danish) (elektronik: [www.dmu.dk/1\\_viden/2\\_Publikationer/3\\_fagrappporter/rappporter/FR421.pdf](http://www.dmu.dk/1_viden/2_Publikationer/3_fagrappporter/rappporter/FR421.pdf)).
- Johnes, P.J., 1996. Evaluation and management of the impact of land use change on the nitrogen and phosphorus load delivered to surface waters: the export coefficient modelling approach. *J. Hydrol.* 183, 323–349.
- Karin Laursen, personal communication. Environmental Protection Agency, Strandgade 29, DK-1401, Copenhagen, Denmark.
- Kronvang, B., Bruhn, A.J., 1996. Choice of sampling strategy and estimation method for calculating nitrogen and phosphorus transport in small lowland streams. *Hydrol. Process.* 1996, 10.
- Kronvang, B., Ærtebjerg, G., Grant, R., Kristensen, P., Hovmand, M., Kirkegaard, J., 1993. Nationwide monitoring of nutrients and their ecological effects: state of the Danish aquatic environment. *AMBIO* 22 (4), 176–187.
- Kronvang, B., Grant, R., Larsen, S.E., Svendsen, L.M., Kristensen, P., 1995. Non point-source nutrient losses to the aquatic environment in Denmark: impact of agriculture. *Mar. Freshwater Res.* 46 (1), 167–177.
- Kronvang, B., Laubel, A.R., Larsen, S.E., Iversen, H.L., Hansen, B.H., 2000. Soil erosion and sediment delivery through buffer zones in Danish slope units, in: Stone, M. (Ed.), The Role of Erosion and Sediment Transport in Nutrient and Contaminant Transfer IAHS 263, pp. 67–73.
- Kronvang, B., Grant, R., Laubel, A.L., Pedersen, M.L., 2002. Quantifying sediment and nutrient pathways within Danish agricultural catchments, in: Haygarth, P.M., Jarvis, S.C. (Eds.), Agriculture, Hydrology and Water Quality. CAB International, pp. 281–301.
- Kronvang, B., Bechmann, M., Pedersen, M.L., Flynn, N., 2003. Phosphorus dynamics and export in streams draining micro-catchments. Development of empirical models. *J. Plant Nutr. Soil Sci.* 166, 469–474.
- Kronvang, B., Jeppesen, E., Conley, D., Søndergaard, M., Larsen, S.E., Ovesen, N.B., this volume. Nutrient pressures and ecological responses to nutrient loading reductions in Danish streams, lakes and coastal waters. *J. Hydrol.*, this volume.
- Laubel, A.R., Kronvang, B., Larsen, S.E., Pedersen, M.L., Svendsen, L.M., 2000. in: Stone, M. (Ed.), The role of erosion and sediment transport in nutrient and contaminant transfer IAHS 263, pp. 75–82.
- Laubel, A., Kronvang, B., Hald, A.B., Jensen, C., 2003. Hydro-morphological and biological factors influencing sediment and phosphorus loss via bank erosion in small lowland rural streams in Denmark. *Hydrol. Process.* 17, 3443–3463.
- Lawler, D.M., 1992. Process dominance in bank erosion systems, in: Carling, P., Petts, G.E. (Eds.), Lowland Floodplain Rivers: Geomorphological Perspectives. Wiley, Chichester, pp. 117–143.
- Loigu, E., 1989. Evaluation of the impact of nonpoint source pollution on the chemical composition of water in small streams and measures for the enhancement of water quality. *River Basin Manag.* 5, 213–217.
- Loigu, E., 1991. The Role of Agriculture and Forestry on the Water Quality of Surface Water in Estonia (In Estonian), Tallinn 1991.
- Miljøstyrelsen, 1999. Punktkilder 1998. Vandmiljøplanens overvågningsprogram: Fagdatacenterrapport. Orientering fra Miljøstyrelsen, 6, 1999 (in Danish).
- Rawlings, J.O., 1988. Applied Regression Analysis. Wadsworth and Brooks/Cole, Belmont, CA.
- Rekolainen, S., 1989. Phosphorus and nitrogen load from forest and agricultural areas in Finland. *Aqua Fennica* 19 (2), 95–107.
- Schoumans, O., Groenendijk, P., 2000. Modeling soil phosphorus levels and phosphorus leaching from agricultural land in the Netherlands. *J. Environ. Qual.* 29, 111–116.
- Sharpley, A., Foy, B., Withers, P., 2000. Practical and innovative measures to control agricultural phosphorus losses to water. *J. Environ. Qual.* 29, 1–9.
- Snedecor, G.W., Cochran, W.G., 1989. Statistical Methods. Iowa State University Press, Ames, Iowa.
- Taylor, R., Flórczyk, H., Jakubowska, L., 1989. Run-off of nutrients from river watersheds used for agricultural purposes. *Environ. Prot. Eng.* 1245065.
- Taylor, R., Flórczyk, H., Jakubowska, L., 1986. Run-off of nutrients from river watersheds used for agricultural purposes. *Environment Protection Engineering* 12 (4), 50–65.