Phosphorus dynamics and export in streams draining micro-catchments: Development of empirical models

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Summary – Zusammenfassung
Annual total phosphorus (TP) export data from 108 European micro-catchments were analyzed against descriptive catchment data on climate (runoff), soil types, catchment size, and land use. The best possible empirical model developed included runoff, proportion of agricultural land and catchment size as explanatory variables but with a low explanation of the variance in the dataset (R² = 0.37). Improved country specific empirical models could be developed in some cases. The best example was from Norway where an analysis of TP-export data from 12 predominantly agricultural micro-catchments revealed a relationship explaining 96% of the variance in TP-export. The explanatory variables were in this case soil-P status (P-AL), proportion of organic soil, and the export of suspended sediment. Another example is from Denmark where an empirical model was established for the basic annual average TP-export from 24 catchments with percentage sandy soils, percentage organic soils, runoff, and application of phosphorus in fertilizer and animal manure as explanatory variables (R² = 0.97).

Phosphordynamik und -verluste aus Kleineinzugsgebieten: Entwicklung von empirischen Modellen
Jährliche Phosphor (P)-Austräge aus 108 europäischen Kleineinzugsgebieten wurden analysiert mit descriptiven Parametern, die Klima, Bodentyp, Größe und Bodennutzung berücksichtigen. Das empirische Modell, welches am besten P-Austräge beschrieb, enthieilt als beschreibende Variablen Wasserausschlag, Anteil an landwirtschaftlich genutzter Fläche und Grösse des Einzugsgebiets. Das Modell konnte jedoch die Varianz der Datenmenge nur ungenügend beschreiben (R² = 0.37). In einigen Fällen konnten verbesserte länderspezifische Modelle entwickelt werden. So wurde für Norwegen ein Modell entwickelt, das für 12 überwiegend landwirtschaftlich genutzte Einzugsgebiete 96 % der Unterschiede der gesamten P-Austräge erklärt. Die Modellvariablen waren in diesem Fall P-Konzentration im Boden (P-AL), Anteil an organischer Bodensubstanz und Abfluss von suspendiertem Material. Ähnlich wurde für Dänemark ein empirisches Modell entwickelt, das mit Hilfe des Anteils an sandigen und humusreichen Bodentypen, des Wasserausflusses und der zugeführten P-Menge den durchschnittlichen P-Austrag aus 24 Wassereinzugsgebieten beschreibt (R² = 0.97).

Key words: phosphorus dynamics / phosphorus export / streams / micro-catchments / empirical models

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1 Introduction
Empirical models of phosphorus (P) delivery to surface water from diffuse sources form an important complement to process-oriented models. Thus, empirical models for diffuse nutrient loadings have been developed based on monitoring data, GIS data on catchment characteristics (soil types, land use, fertilization level, etc.), and climate characteristics from meso-catchments and micro-catchments in many European countries (Kronvang et al., 1995; Johnes et al., 1996; Ekholm et al., 2000). However, existing data from European catchments have not yet been fully exploited. In particular, substantially more can be done to scrutinize observed data in a European perspective for use in an empirical modeling approach on climate (drought and floods) and agricultural impacts (croptype, land management) on extreme phosphorus concentrations and loads. Phosphorus is much more vulnerable to extreme climatic events than nitrogen due the former being mobilized and delivered in substantial quantities from erosional processes and linked hydrological pathways (soil erosion, preferential flow in soils and bank erosion) (eg. Kronvang et al., 2002).

Intensive measurements of phosphorus concentrations exist from many streams monitoring and research programs in the European countries. Such data can in a novel approach be used to learn about micro-catchment (< 100 km²) responses to differences in climate, soil types, land use, agricultural practices, etc.

In this paper we utilize data on annual P-export from 114 European micro-catchments, 12 Norwegian micro-catchments, and 24 Danish micro-catchments for development of empirical annual total P-export models.

2 Study catchments
Data from a total of 114 micro-catchments (< 100 km²) were supplied by ten countries being members of the EU-COST Action 832 on Phosphorus Losses from Agriculture for inclusion in a catchment database. Table 1 summarizes the information collected from each of the contributing countries. Six out of the ten countries have micro-catchments included in their monitoring programs, of which four are national programs (Denmark, Finland, Norway, and Sweden). The monitoring periods of all of the catchments range in time scale from 1 to 20 years. The catchment type is divided into agricultural (> 50% agricultural land), mixed (10–50% agricultural land), or natural (< 10% agricultural land). As evident in Tab. 1, most of the monitored catchments are agricultural or

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mixed. In Denmark 24 agricultural dominated micro-catchments was included in a country specific empirical modeling approach and in Norway 12 agricultural dominated micro-catchments.

3 Methodology

The type of water sampling carried out in the countries surveyed was either as manual point sampling, automatic composite sampling or a combination of both. All of the countries, with the exception of Austria, use automatic composite sampling, either as time equidistant, flow proportional or both. The majority of the countries also use manual point sampling, and in five out of the ten countries, mixed sampling is used (manual point and either time equidistant or flow proportional composite sampling).

Discharge measurements occur as either fixed structure measurements or natural profile measurements in the streams draining the catchments. The frequency of stage recording is continuous in most countries, with less frequent measurements for discharge. The accuracy of the calculated daily discharge ranges up to ±25%.

All countries analyzed for total P (TP). Most of the countries used linear interpolation between observations of P concentrations multiplied by daily discharge to obtain the daily, monthly and annual P transport. The accuracy of the annual P transport calculated was estimated to be ±20–40 % in Denmark, and ±10–30 % in Ireland.

4 Results

4.1 The dynamics of phosphorus concentrations and loads in streams

Experience from a small Danish stream being sampled very intensively (minutes, hour) show the very dynamic nature of phosphorus concentrations during rain events (Fig. 1). The P

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<table>
<thead>
<tr>
<th>Countries</th>
<th>Number of catchments</th>
<th>Agricultural</th>
<th>Mixed</th>
<th>Natural</th>
<th>Time series length</th>
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<tr>
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<td>2</td>
<td>2</td>
<td></td>
<td></td>
<td>1–3 years</td>
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<tr>
<td>Denmark</td>
<td>45</td>
<td>34</td>
<td>7</td>
<td>4</td>
<td>1989+</td>
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<tr>
<td>Finland</td>
<td>15</td>
<td>3</td>
<td>3</td>
<td>9</td>
<td>1965+ or 1981+</td>
</tr>
<tr>
<td>Germany</td>
<td>3</td>
<td>1</td>
<td>2</td>
<td></td>
<td>&lt; 1 year</td>
</tr>
<tr>
<td>Netherlands</td>
<td>2</td>
<td>1</td>
<td></td>
<td>1</td>
<td>3 and 6 year</td>
</tr>
<tr>
<td>Norway</td>
<td>10</td>
<td>6</td>
<td>4</td>
<td></td>
<td>6–15 years</td>
</tr>
<tr>
<td>Rep. of Ireland</td>
<td>3</td>
<td>3</td>
<td></td>
<td></td>
<td>1–20 years</td>
</tr>
<tr>
<td>Spain</td>
<td>3</td>
<td>1</td>
<td></td>
<td>2</td>
<td>2 to 20 years</td>
</tr>
<tr>
<td>Sweden</td>
<td>23</td>
<td>21</td>
<td>2</td>
<td></td>
<td>1988 or 1993+</td>
</tr>
<tr>
<td>UK</td>
<td>5–8</td>
<td>5–8</td>
<td></td>
<td></td>
<td>3–6 years</td>
</tr>
<tr>
<td>Total</td>
<td>111–114</td>
<td>76–79</td>
<td>19</td>
<td>16</td>
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</tr>
</tbody>
</table>

Figure 1: Concentration of different phosphorus fractions (P) and runoff (Q) during three single storm events on different times of the year in a Danish lowland stream draining a 10 km² catchment. DRP: Dissolved Reactive P; PIP: Particulate Inorganic P; POP: Particulate Organic P; PP: Particulate P; DOP: Dissolved Organic P. Abbildung 1: Gehalte unterschiedlicher P-Fraktionen (P) in und Oberflächenabfluss (Q) aus einem Oberflächengewässer im dänischen Flachland (10 km² Einzugsgebiet) während dreier einzelner Starkniederschlagsereignisse zu unterschiedlichen Zeiten des Jahres. DRP: Gelöster reaktiver P; PIP: Partikulärer anorganischer P; POP: Partikulärer organischer P; PP: Partikulärer P; DOP: Gelöster organischer P.
concentration response to rain and hence increasing discharge in the stream differs considerably during the year with highest P concentrations reached during early autumn where phosphorus retained during the low-flow summer period was flushed out of the catchment.

In Norway snowmelt cause surface runoff and erosion during winter/spring leading to high concentrations of TP. Thus, 60% of the annual TP-export occurred in the period from January to April in the Skuterud Catchment (Bechmann et al., 1999). Particulate P fractions are in many cases dominant for the total P-export from smaller catchments. Therefore, the P concentration and P-export from small catchments is much more episodic in nature than in larger catchments as shown in Fig. 2 for two different sized Danish lowland catchments. The P-export from small catchments differs also considerably from year to year as shown for 7 intensively (timeproportional or flowproportional) sampled small Danish catchments in Fig. 3. The differences in annual P-export from the 7 Danish catchments could to a large extent be explained by differences in annual runoff ($R^2 = 0.71$).

Figure 2: Concentrations of total phosphorus in two Danish lowland streams during a two months period.

Abbildung 2: Konzentrationen an Gesamt-P in zwei Flussläufen im dänischen Flachland im Verlauf von zwei Monaten.

Figure 3: Annual average total phosphorus export and runoff from 7 Danish lowland streams draining agricultural dominated microcatchments during the period 1993–2001.


4.2 Relationships between P-export and catchment characteristics across all European countries

The COST ACTION database was used to determine whether any relationships existed between phosphorus export and catchment variables such as runoff, catchment size, soil types or percentage of arable land.

No clear relationship was apparent between TP-export and runoff when plotting the data in a scatterplot for the microcatchments (Fig. 4). Catchment size and soil type showed, however, interesting results when plotted against P-export. Catchment size was divided into three size groups (Fig. 5). The range of TP-export and flow-weighted TP-export values were then plotted for these groups. Although the average figures (displayed on the bars) were quite similar, it seem that

Abbildung 4: Beziehung zwischen dem mittleren jährlichen diffusen Austrag an Gesamt-P und dem mittleren jährlichen Oberflächenabfluss in 114 europäischen Kleineinzugsgebieten.

Abbildung 5: Mittlere diffuse Gesamt-P-Austräge aus Kleineinzugsgebieten in: A: P-Austrag in kg ha⁻¹; B: Abflussbezogener P-Austrag in kg (ha 100 mm Oberflächenabfluss)⁻¹.
smaller catchments experience the highest maximum values of flow-weighted TP-export, and larger catchments the lowest maximum values.

When soil type was plotted with TP-export and flow-weighted TP-export, the pattern is very different as is apparent in Fig. 6. The average TP-export did not reveal any substantial differences. On contrary, the average flow-weighted TP-export revealed quite large differences the sandy catchments having half the flow-weighted TP-export than that of the loam and clay catchments. In addition, the sandy catchments have the lowest maximum values of TP-export, being approximately half of the maximum values for loam dominated catchments, and also lower than that for the clay catchments.

![Bar charts of diffuses total phosphorus export compared to four dominant soil classes in the catchments.](image)

**Figure 6:** Average diffuse total phosphorus export as compared to four dominant soil classes in the catchments. A: P-export in kg ha⁻¹; B: Flow-adjusted P-export in kg (ha 100 mm runoff)⁻¹.

Abbildung 6: Mittlere diffuse Gesamt-P-Austräge von vier wichtigen Bodensubstraten in den Einzugsgebieten. A: P-Austrag in kg ha⁻¹; B: Abflussbezogener P-Austrag in kg (ha 100 mm Oberflächenabfluss)⁻¹

Average annual diffuse total phosphorus export was plotted against the percentage of arable land for all countries in Figure 7A. It is evident that there is a large scatter, with the bulk of the highest average annual TP-export occurring with over 30% arable land (Fig. 7A). However, there are some very high values (including the highest value from the dataset) where there is a low percentage of arable land. This pattern changes somewhat when the flow-weighted TP-export is plotted against arable land (Fig. 7B). A significant relationship is clearly not present. However, a division of the dataset at a threshold of 40% agricultural land revealed that those catchments containing < 40% arable land experienced a much lower TP-export value (0.12 kg P ha⁻¹ per 100 mm), compared to the catchment having > 40% agricultural land (0.30 kg P ha⁻¹ per 100 mm) (Fig. 7B).

![Graph showing relationship between diffuse P-export and percentage arable land.](image)

**Figure 7:** Relationship between average annual diffuse total P-export and percentage of arable land within 137 micro-catchments in European countries.

Abbildung 7: Beziehung zwischen dem jährlichen mittleren diffusen Gesamt-P-Austrag und dem Anteil an Ackerfläche in 137 Kleineinzugsgebieten in Europa.

An empirical model (1) was developed based on the average annual TP-export data from 108 of the micro-catchments:

\[
\ln(P_{\text{kg/ha}}) = -2.96 + 0.0156(AL_{\%}) + 0.0024(R_{\text{mm}}) + 0.0145(CA_{\text{km}^2})
\]

Where \( P_{\text{kg/ha}} \) = Annual total P-export (kg P ha⁻¹); AL = percentage agricultural land (%); \( R \) = runoff (mm); CA = catchment area (km²).

N = 108; \( R^2 = 0.37; P < 0.001. \)

Relationships between diffuse TP-export and percentage arable land were developed for individual countries (Fig. 8). Data from some of the countries showed significant relationships (micro-catchments from UK, micro-catchments from Finland, and micro-catchments from Denmark) (Fig. 8). The

![Graph showing relationships between total phosphorus export and percentage arable land for micro-catchments in four different European countries.](image)

**Figure 8:** Relationships between total phosphorus export and percentage arable land for micro-catchments in four different European countries.

Abbildung 8: Beziehungen zwischen den Gesamt-P-Austrägen und den Anteilen an Ackerfläche in Kleineinzugsgebieten in vier unterschiedlichen europäischen Ländern.
poor relationship developed when utilizing data from all 10 countries can be seen in Fig. 7 where large and as yet unexplainable deviations in the annual TP-export level exists between the countries. One possible explanation could be differences in the extent of critical source areas linked to hydrological pathways in the countries.

4.3 An empirical TP-export model for Danish and Norwegian micro-catchments

The annual total P-export data from 24 Danish agricultural dominated micro-catchments was recalculated in a way to remove the impact of episodic runoff events. A hydrograph separation technique enabled us to remove the P concentrations measured under storm runoff events. Therefore, the resulting total P-export was a basic P-export without major influence from erosional P sources. A stepwise multiple regression model was developed from these annual basic TP-export data (2):

\[
P_{\text{kg/ha}} = -0.00191(S_s) + 0.00605(\text{OSA}) + 0.000648(R) + 0.01164(P_s) \tag{2}
\]

Where \( S_s \) = percentage sandy soils in the catchment; \( \text{OSA} \) = percentage organic soils in the catchment; \( R \) = annual runoff (mm); \( P_s \) = average application of phosphorus on agricultural land but transferred as an average input to the entire catchment area (kg P ha\(^{-1}\)).

\[N = 24; R^2 = 0.97; P < 0.05.\]

The Norwegian micro-catchments experienced in general the highest average annual TP-export of all the countries examined and revealed also the poorest relationship to percentage agricultural land (Fig. 8).

However, a detailed investigation of the Norwegian data including descriptive parameters as soil-P status, P fertilizer, P manure, catchment area, organic soil, and export of suspended solids as an indirect measure of soil erosion showed that the relationship could be improved. Thus, a multiple regression analysis resulted in three variables being statistically significant in explaining the average annual TP-export (3):

\[
P_{\text{kg/ha}} = -0.45 + 0.07(\text{P-AL}) + 0.001(\text{SS}) + 0.13(\text{OSA}) \tag{3}
\]

Where \( P_{\text{kg/ha}} \) = Annual total P-export (kg P ha\(^{-1}\)); \( \text{P-AL} \) = soil P content (mg (100 g)\(^{-1}\)); \( \text{SS} \) = annual suspended sediment export (kg ha\(^{-1}\)); \( \text{OSA} \) = organic soil area (%). \( N = 12; R^2 = 0.96; P < 0.05.\)

The inclusion of the export of suspended sediment as an explanatory parameter clearly indicates the importance of erosion for total P-export in Norwegian catchments. Suspended sediment could easily and without major costs be continuously monitored by applying a turbidity meter in the stream. In that case, the above model could help to obtain more precise total P-exports.

5 Discussions and conclusions

Research on diffuse losses of phosphorus from European catchments has evolved during the last decade because phosphorus is a key limiting macro-nutrient in freshwater systems (Vollenweider, 1976; Jeppesen et al., 1999; Kronvang et al., 2002). Our ability to quantify and describe the dynamics of phosphorus export has been debated and several studies have focused on the methodological approaches for sampling techniques, sampling frequency, etc. (Kronvang and Bruhn, 1996). Most of the studies hitherto conducted have been on a national scale that may limit their application to other landscapes, climate regions, etc. We collected data and established a database with data on phosphorus export and catchment characteristics covering several European countries for use in analyzing diffuse total P-export from micro-catchments.

In general, we found that the diffuse total phosphorus export from micro-catchments experienced very poor relationship to catchment characteristics as runoff, soil type and land use (Fig. 4, 5, and 6). However, utilization of the flow-weighted total P-export improved the relationships to catchment size, soil type and land use characteristics (Fig. 5, 6, and 7).

The flow-weighted diffuse total P-export from micro-catchments was significantly higher for catchment having a percentage of arable land > 40% (0.30 kg P ha\(^{-1}\) (100 mm)\(^{-1}\)) than for catchments having a percentage of arable land < 40% (0.12 kg P ha\(^{-1}\) (100 mm)\(^{-1}\)).

We developed a significant empirical model for the diffuse annual TP-export based on data from 108 micro-catchments in European countries. The empirical model includes arable land, runoff, and catchment size as explanatory variables having a reasonable poor predictive power. Stronger relationships between diffuse TP-export and percentage arable land were developed for micro-catchment in some of the countries (Fig. 8). This is in accordance with the findings in several other studies where relationships for the diffuse TP-export has been developed on a regional or national scale (Rekolainen, 1989; Kronvang et al., 1995; Ekholm et al., 2000).

The large difference in diffuse TP-export from micro-catchments between the countries is one of the main reasons for the difficulties observed in developing strong empirical models (Fig. 8). These differences are not explained by the explanatory variables involved in this study. Some of the variation in TP-export between countries may also be attached to differences in monitoring strategies. Another possible explanation could be that large differences exist in the management of animal manure and in the extent of critical source areas linked to hydrological pathways between the countries.

The reason for the difficulties involved when trying to develop empirical TP-export models for micro-catchments are undoubtedly the many transport processes linking P source areas to surface waters (Kronvang et al., 2002). In sloping areas soil erosion may be determinant for TP-export, and both landscape characteristics and agricultural management...
practice may be more important for TP-export than the included explanatory variables. Moreover, both depositional and sorption processes are active along the P transport route from source area to surface water hence affecting the resulting quality and quantity of phosphorus exported from catchments.

We utilized data from the Danish and Norwegian monitoring program to investigate in more detail the possibility of modeling annual TP-export from micro-catchments. The Danish P-export data was re-calculated to assure that P concentrations during storm events were extracted from the annual transport estimate. A significant empirical model for this basic TP-export from the catchments was established with percentage sandy soils, percentage organic soils, runoff, and application of phosphorus in fertilizer and animal manure as explanatory variables ($R^2 = 0.97$).

In the case of the Norwegian micro-catchments, we developed a significant empirical model that enabled us to predict the diffuse annual average TP-export. The model included soil P content, suspended sediment export, and organic soil area as explanatory variables ($R^2 = 0.96$). The suspended sediment export and percentage of organic soils in the catchments revealed nearly the same strong correlation ($R^2 = 0.52$) to average annual TP-export from the 12 catchments. Clearly this shows the importance of two different processes affecting the resulting TP-export namely particulate P delivery from soil erosion and overland flow and leaching of dissolved P from low P-adsorptive organic soils.

This study clearly shows that we need to have a more thorough knowledge on source areas and transport processes linking source areas to surface waters in catchments in order to improve our ability to develop empirical models for TP-export from micro-catchments. Such models are useful as screening tools in larger river basins when analyzing the pressure/impact of phosphorus under the EU-Water Framework Directive. In a later stage other types of models are needed for development of management plans where specific mitigation measures in source areas and towards transport processes have to be implemented in the catchment. Such models could be simple P-index models or more process-oriented P-models (Heathwaite et al., 2003).

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References


