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# Bayesian estimation of export coefficients from diffuse and point sources in Swiss watersheds

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**Summary** By combining prior knowledge with data from 11 watershed outlets in Switzerland we estimated export coefficients for soluble reactive phosphorus (SRP), nitrate, total nitrogen, chloride, potassium and alkalinity from different land use categories over a 24 year investigation period. The analysis clearly attributes the observed reduction of SRP loads in the rivers to a decrease in contributions from urban areas from about 0.5 to about 0.04 kg P $inhab^{-1}\,a^{-1}$ between 1980 and 1990. This reflects measures taken to reduce phosphate discharge from urban areas into receiving water bodies and it significantly increases the relative contribution from intensively used agricultural land (about 0.03 g P $m^{-2}\,a^{-1}$) to total SRP load. At the relatively coarse resolution level of this study, there was no significant trend in any of the other export coefficients. Dominant sources of nitrate, chloride and potassium are intensive agriculture with contributions of about 2.9 g N $m^{-2}\,a^{-1}$, 8.7 g Cl $m^{-2}\,a^{-1}$, and 1.9 g K $m^{-2}\,a^{-1}$, and urban diffuse and point sources with contributions of about 2.1 kg N $inhab^{-1}\,a^{-1}$, 20 kg Cl $inhab^{-1}\,a^{-1}$, and 2.5 kg K $inhab^{-1}\,a^{-1}$. Contributions from intensively used agricultural land are significantly higher than the background exports from extensively used land, forests and barren land which are in the order of 0.5 g N $m^{-2}\,a^{-1}$, 1.1 g Cl $m^{-2}\,a^{-1}$ and 0.6 g K $m^{-2}\,a^{-1}$ (2.2 for barren land). Dependence of alkalinity exports on land use was much smaller with contributions between 1.6 and 3.8 mol $m^{-2}\,a^{-1}$. From a methodological point of view, our results reveal that Bayesian inference is an excellent mathematical framework to overcome the identification problems resulting from a partially ill-defined regression problem if prior knowledge is available.


## Introduction

Comprehensive and expensive measures implemented over the past decades for reducing pollutant discharge to surface waters should lead to improved water quality. Data from

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long-term monitoring programmes of constituents in natural waters should reflect such changes. However, it is often difficult to detect such changes and to uniquely attribute them to specific measures. Reasons for these difficulties are the large number of inputs, their high temporal and spatial variability, changes in concentration due to dilution and transformation processes, and long response times of some of the involved sub-systems of the watershed (particularly soil and groundwater).

The current study aims at evaluating the contributions of different inputs to loads and concentrations at watershed outlets belonging to the Swiss long-term monitoring program. This knowledge can contribute to improving our understanding of processes in the watershed and our design of measures for reducing surface water pollution. With respect to water quality parameters we focus on soluble reactive phosphorus (SRP), nitrate, chloride, potassium and alkalinity. These compounds were selected according to the following criteria: (i) consideration of the most relevant nutrients, (ii) extension to compounds that are of geochemical interest, and (iii) limitation to dissolved compounds to allow for a simple model structure (total nitrogen was added later on; primarily due to the dominance of nitrate, it still fitted well into the approach). For these compounds, the following goals had to be addressed:

- gain of a quantitative understanding of differences in concentrations at different watershed outlets and of contributions of different categories of sources to total loads;
- identification of temporal trends and attribution to management measures taken during the past 24 years (the time span of available data);
- support of decisions about future measurement sites of the Swiss National River Survey Programme (NADUF; http://www.naduf.ch);
- provision of a simple tool for estimating the effect of land use change on river water quality.

To address these goals, we need a quantitative parameterization of the watershed outlet concentrations or loads as functions of the most relevant influence factors. These concentrations and loads are influenced by point sources discharging into the rivers; diffuse inputs to the rivers associated with surface runoff, drainage, lateral transport in soils, groundwater exfiltration, and chemical and biological transformation processes in the river. Inputs from point sources are strongly related to the population living in the watershed, to the degree and type of industrialization, and to the level of sewage treatment. Inputs from diffuse sources depend on land use and management, rain intensity, the topography of the watershed, and soil properties. The task of relating measured substance concentrations to specific inputs from anthropogenic and natural sources led to the development of watershed models of different levels of complexity.

Detailed representations of input, transfer and transformation of substances of relevance for water quality within a watershed have been developed in the form of detailed, mechanistic hydrological and water quality models. Examples of computer programs implementing such models are the Agricultural Non-Point Source model (AGNPS; Young et al., 1989) and the Soil and Water Assessment Tool (SWAT; Arnold et al., 1998). After calibration to a specific watershed, such models can in principle be used to predict the effect of land use and land management change on water quality in the rivers. However, such models need a huge amount of input data. Required data include topographic information in the form of a digital elevation map, a soil map and corresponding information on hydrologically relevant parameters, a land use map and information on cultivation practice (such as seeding and harvest times, crop types, fertilization, tillage, application of pesticides, etc.), data on precipitation, temperature, global or photosynthetically active radiation, locations and discharge characteristics of point sources, and management information on artificially controlled water bodies. These extensive input requirements make such a modelling task a highly demanding project. Despite the use of detailed input data, the remaining need for spatial and temporal interpolation of point measurements still lead to high input uncertainty. This is particularly true for precipitation, soil properties, and transformation rates. Up-scaling of process descriptions to sub-watershed computational elements cause similar uncertainties in model formulation and effective parameter values. Therefore, despite the detailed and mechanistic description of the most important processes, such models still face a high prediction uncertainty. Nevertheless, due to their process-oriented approach, mechanistic watershed models will certainly continue to play an important role in watershed scale research and management.

However, the problems mentioned above raise the need for alternative approaches to complement detailed mechanistic modelling. These approaches rely on less complex procedures for estimating contributions of different sources to observed concentrations in rivers and for estimating the effect of land use or land management change on these concentrations. Several such alternatives have been developed over the past 30 years. They can be used for preliminary assessments and for areas at which the limited information makes it too difficult to apply a detailed mechanistic watershed model.

Simpler alternatives to mechanistic watershed modelling use parameterizations of output concentrations or loads as functions of the most important influence factors. The parameters of these models are then estimated by applying statistical techniques. Two approaches can be distinguished:

(i) The first approach parameterizes watershed outlet concentrations or loads of a compound as a function of input. Parameters of such a model, such as transfer coefficients from an agricultural field to a river, can be estimated based on input data and observed concentrations at the watershed outlet. If this is not possible, transfer coefficients estimated for a similar watershed, or for the same watershed under previously observed different input loads, can be used as prior knowledge (e.g. Prasuhn and Braun, 1994; Smith et al., 1997; Prasuhn, 1999; Schmid and Prasuhn, 2000).

(ii) The second approach is even simpler. It assigns so-called export coefficients, as mass discharged per area and time, to typical land use categories in the watershed, and adds the total load by summing up all of these contributions. Export coefficients are usually estimated from measured concentrations in rivers draining (small) watersheds of uniform land use (e.g. Beaulac and Reckhow, 1982; Clesceri et al., 1986; Frink, 1991).

Similarly to mechanistic watershed modelling, the first approach attempts to derive parameters that are not sensitive to changes in input. For this reason, it is more appropriate for predicting the effect of changes in input. The export coefficients used in the second approach describe the input together with the effect of transfer and transformation processes implicitly. This makes their values much less universal. On the other hand, determination of export coefficients from river concentration data provides integral information on the effect of all factors influencing the discharge into the river. For this reason, export coefficients estimated from river water quality data are good indicators to address the question whether there was a significant change in pollutant discharge into the river. This is the reason, why we are using export coefficients in the current study.

Export coefficients have been applied in many studies of watershed data over the past decades (e.g. Beaulac and Reckhow, 1982; Clesceri et al., 1986; Frink, 1991). This study adds interesting methodological aspects to what has been done before:

- using long-term, high-quality (continuous and flow proportional sampling) data from Swiss watersheds (so far most applications have used grab sampling data);
- investigating temporal change in export coefficients (so far most analyses were done for a single time period);
- applying the approach to several substances of anthropogenic and geogenic origin (so far most applications were done for nitrogen and phosphorus only);
- dealing jointly with several heterogeneous watersheds consisting of all types of land use, e.g. diffuse and point sources (so far most analyses were done for watersheds that were dominated by a single land use category);
- explicitly considering prior knowledge of typical values of export coefficients (derived from small watersheds with a single dominating land use category), by performing a Bayesian, in addition to a frequentist, analysis (so far prior knowledge was mostly only used for discussing the results).

The discussion of these points may stimulate the transfer of methodological aspects raised in this paper to further studies in this field.

## Data analysis techniques

### Modelling approach

The loads of chemical substances transported in a river result from diffuse inputs, discharge from point sources, and transformation processes in the river. The simplest model (ii) mentioned in the introduction assumes that average diffuse loads can be estimated by a sum of terms proportional to different land use types with land use and substance specific export coefficients (e.g. Beaulac and Reckhow, 1982; Clesceri et al., 1986; Frink, 1991). In analogy to this description of diffuse sources, the inputs from point sources can be assumed to be proportional to the number of inhabitants in the watershed. When formulating this model for temporally averaged loads from a number of watersheds, we obtain the following equation:

$$L_j^{\text{mod}}(\boldsymbol{\theta}) = \theta_0 \cdot n_j + \sum_{i=1}^{n_{\text{lu}}} \theta_i \cdot A_{i,j} \tag{1}$$

where $j$ is the index labelling the watershed, $i$ is the index labelling the land use types, $L_j^{\text{mod}}$ is the average load at the outlet of watershed $j$ as predicted by the model, $n_j$ is the number of inhabitants of watershed $j$, $n_{\text{lu}}$ is the number of land use categories considered by the model, $A_{i,j}$ is the area of land use category $i$ in watershed $j$, and $\boldsymbol{\theta} = (\theta_0, \ldots, \theta_{n\text{lu}})$ are the export coefficients for inhabitants ($i = 0$) and land uses 1 to $n_{\text{lu}}$ (if $i = 0$ specified as mass per number of inhabitants and year, else as mass per surface area of land use type $i$ and year). When predicting concentrations instead of loads, the model equation must be modified as follows:

$$C_j^{\text{mod}}(\boldsymbol{\theta}) = \frac{\theta_0 \cdot n_j + \sum_{i=1}^{n_{\text{lu}}} \theta_i \cdot A_{i,j}}{Q_j} \tag{2}$$

where $C_j^{\text{mod}}$ is the concentration at the outlet of watershed $j$ as predicted by the model, $Q_j$ is the discharge at the outlet of watershed $j$, and the other symbols have the same meaning as in Eq. (1).

As export of pollutants to rivers is a highly dynamic process dominated by short periods of time during flood events, the simple models formulated by Eqs. (1) and (2) can only be applied when the data is averaged over time periods that contain many such events. For this reason, we will apply the model to 5 year running averages of yearly loads and concentrations.

When assuming normally and independently distributed stochastic errors that add to the results of the deterministic functions given by the Eqs. (1) and (2), the likelihood functions of our two models for loads and concentrations become

$$f_y(\mathbf{y}|\boldsymbol{\theta}, \sigma_y) = \frac{1}{\sqrt{2\pi}^{n_w}} \frac{1}{\sigma_y^{n_w}} \exp\left(-\sum_{j=1}^{n_w} \frac{(y_j - y_j^{\text{mod}}(\boldsymbol{\theta}))^2}{2\sigma_y^2}\right) \tag{3}$$

where $\mathbf{y} = (y_1, \ldots, y_{\text{nw}})$ is the vector of loads or concentrations of all watersheds, $\sigma_y$ is the standard deviation of the normal distribution of loads or concentrations around the deterministic model results, $n_w$ is the number of watersheds, and $y_j^{\text{mod}}$ is either $L_j^{\text{mod}}$ or $C_j^{\text{mod}}$ according to Eqs. (1) or (2), respectively.

### Estimation of export coefficients

Usually, export coefficients are determined with the aid of load measurements at outlets of watersheds with a single dominant land use. In the present study we use watersheds associated with measurement sites of the Swiss National River Survey Programme (NADUF; http://www.naduf.ch).

These watersheds contain land uses of all categories. To be able to estimate the export coefficients in such a setting, we assume that the export coefficients for the same land use category are the same in all watersheds. This is a reasonable assumption as the model is applied to a region with similar wastewater treatment technology, topographic characteristics, soil properties, climatic conditions, and land management practice. If the area fractions of different land use categories are varying between watersheds we can then determine export coefficients by a joint regression analysis for all watersheds. We will apply a frequentist and a Bayesian technique to estimate export coefficients for multiple watersheds.

The frequentist approach has the goal of extracting information from data only, without relying on prior knowledge, with the exception of the knowledge used to set up the model equations. For this approach, the parameter estimates are determined by maximization of the likelihood function (3) into which measurements are substituted for the argument describing the outcomes:

$$(\hat{\boldsymbol{\theta}}, \hat{\sigma}_y) = \arg\ \max_{(\boldsymbol{\theta},\sigma_y)\geqslant 0} f_y(\mathbf{y}^{\text{meas}}|\boldsymbol{\theta}, \sigma_y) \tag{4}$$

In this equation, $\hat{\boldsymbol{\theta}}$ are the estimates of the export coefficients $\boldsymbol{\theta}$ as introduced in Eqs. (1) and (2), $\hat{\sigma}_y$ is the estimate of the standard deviation of the additive stochastic error term $\sigma_y$ introduced in Eq. (3), $f_y$ is the likelihood function of the model as given by Eq. (3), and $\mathbf{y}^{\text{meas}}$ are the measured concentrations or loads at the watershed outlets.

The interpretation of the model parameters as export coefficients (see Eqs. (1) and (2)) makes negative values unreasonable. For this reason, it is meaningful to apply the condition of non-negative parameter values as a constraint for the maximization process in Eq. (4). We applied the routine **pcls** (Wood, 1994) from the package **mgcv** of the statistics and graphics tool R (Ihaka and Gentleman, 1996; http://www.r-project.org) to perform the constrained minimization (Gill et al., 1981). The frequentist approach (4) requires a well-defined maximum of the likelihood function in order to provide unique results. If this maximum is only poorly defined, minor changes in data may cause significant changes in parameter estimates and numerical algorithms can have problems finding the maximum.

In contrast to the frequentist approach, the Bayesian approach has the goal of combining prior knowledge with data to optimally use both sources of information. Prior knowledge on parameter values has to be formulated as a prior probability density, $f_{\text{pri}}(\boldsymbol{\theta},\sigma_y)$, and is then updated to the posterior density by applying the equation

$$f_{\text{post}}(\boldsymbol{\theta}, \sigma_y|\mathbf{y}^{\text{meas}}) \propto f_y(\mathbf{y}^{\text{meas}}|\boldsymbol{\theta}, \sigma_y) \cdot f_{\text{pri}}(\boldsymbol{\theta}, \sigma_y) \tag{5}$$

where the constant of proportionality is calculated by normalization of the posterior density. This technique has the advantage of still being applicable if the parameters are not identifiable from the data. In case of poor identifiability, the posterior distribution is not much different from the prior. In case of high information content of the data, it is typically much narrower. The disadvantage of this technique is that use of prior information introduces a subjective element into the data evaluation procedure. The severity of this disadvantage depends on the justifiability of the prior distribution.

To get a numerical approximation to the posterior distribution (5), a sample was calculated by applying a Markov Chain Monte Carlo technique (Gelman et al., 1995; Gamerman, 1997) as implemented in the UNCSIM package (Reichert, 2005; http://www.uncsim.eawag.ch). The starting point for the Markov Chain was selected by maximizing the posterior to avoid long burn-in periods. Two chains of a length of 25,000 points each (plus 10% that were later dropped to eliminate effects of a burn-in phase on inference results) were created, the first using an uncorrelated multivariate normal jump distribution, the second using the correlation matrix of the posterior from the first chain as the correlation matrix for the jump distribution. The step size of the jump distribution was adjusted to lead to an acceptance rate in the order of 20%.

## Data

### Watershed characteristics

Discharge and water quality data were provided by the Swiss National River Survey Programme (NADUF; http://www.naduf.ch). In this programme (Jakob et al., 2002), nutrients, geochemical parameters and contaminants have been measured in biweekly, flow proportional, composite samples at hydrometric stations at the main Swiss rivers since 1974. This sampling technique is providing proper loads.

To guarantee approximate statistical independence of watersheds only data from those NADUF stations were used which did not contribute more than 20% to the watershed of another station. To fulfil the assumption of approximate homogeneity in geology and climatic conditions, only the stations to the north of the Alps were considered. The degree of connection of households to sewage treatment plants and agricultural practices on fields exposed to similar environmental condition, both do not vary strongly between the investigated watersheds. However, there are significant differences in land use climate conditions between lowland and alpine regions. This leads to different fractions of land use categories. Despite these arguments for homogeneity, remaining differences in soil properties, agricultural practices and local variations in climate conditions between watersheds are certainly a major reason for the scatter of measured data around model results. Fig. 1 gives an overview of location and extent of the watersheds of the measurement sites used for the current study.

Land use data was provided by the national area statistics of 1982 (1979–1985) and 1995 (1992–1997) (Swiss Statistics). Land use data were aggregated from 74 to five categories based on typical fertiliser use and land cover (Table 1). These data were linearly inter- and extrapolated to the investigation period (1980–2003). For most watersheds, the fractions of intensively used agricultural land and barren land decreased over time, whereas the fractions of the other categories increased. These changes varied between $-4.5‰$ and $+2.1‰$ per year at most.

Population data for watersheds were calculated from community records of the national census data of 1990 and later adjustments (Swiss Statistics). The national popu-

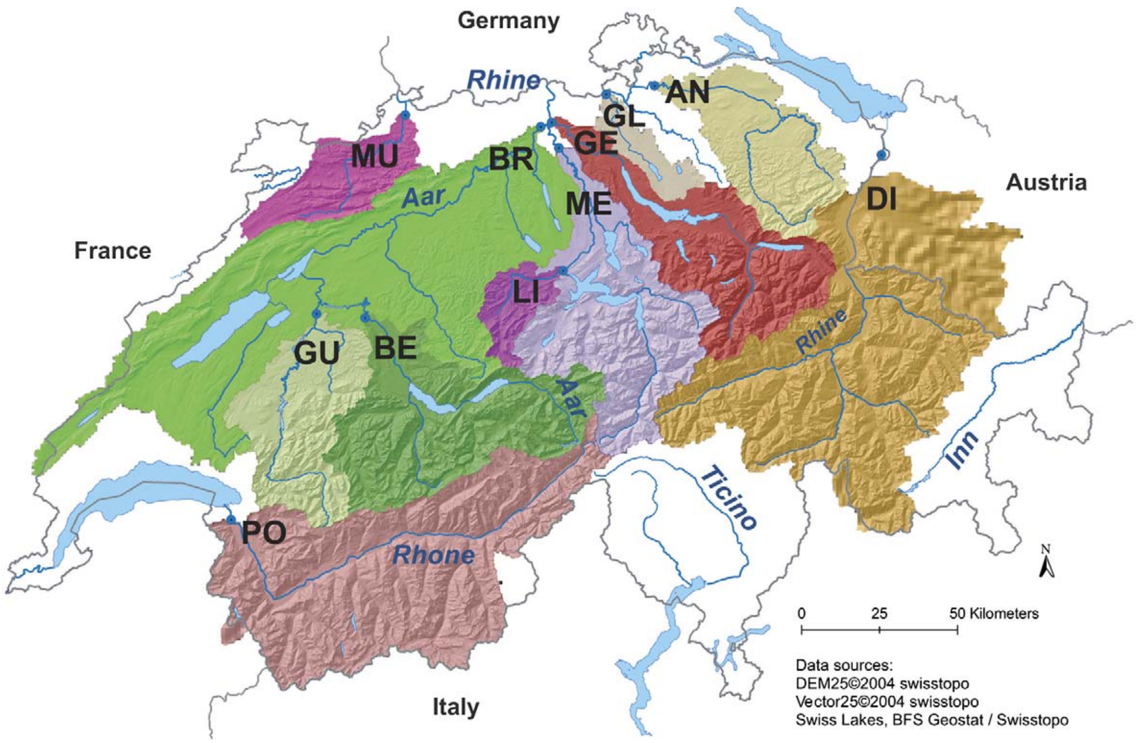


**Figure 1** Map of the Swiss surface waters and the watersheds used for the analysis (see text for the selection criteria). The following measurement sites of the Swiss National River Survey program (NADUF, http://www.naduf.ch) were used: DI = Rhine River at Diepoldsau, AN = Thur River at Andelfingen, GL = Glatt River at Rheinsfelden, BE = Aare River at Bern, GU = Saane River at Guemmenen, BR = Aare River at Brugg, LI = Kleine Emme River at Littau, ME = Reuss River at Melligen, GE = Limmat River at Gebenstorf, MU = Birs River at Muenchenstein, PO = Rhone River at Porte-du-Scex.

**Table 1** Land use categories and their abbreviations as used in this paper

| Abbreviation | Land use category |
|---|---|
| Agriint | Intensively used agricultural land (fertilized land) |
| Ext | Extensively used land (mainly grass- and bush land, alpine pasture) |
| Forest | Dense forest |
| Barren | Barren land including surface waters (small fraction) |
| Inhab | Number of inhabitants (urban land (settlements and traffic ways) could be used instead, as this correlates very strongly with the number of inhabitants with an average population density of 2300 persons per km$^2$ of urban land) |

lation increase of 4.7‰ per year was used to estimate population increase in all watersheds. Using the number of inhabitants in a watershed to approximate the contribution by point sources seems to be justified for our study. In the year 2000, more than 95% of the population were connected to wastewater treatment plants with similar removal rates for pollutants (1980 there were about 80% connected). In addition, in the watersheds and for the compounds considered, there are no large industrial plants that would lead to discharges deviating from the proportionality to population (except for chloride in the alpine Rhone watershed).

Fig. 2 summarizes the areas, land use fractions, numbers of inhabitants, and specific discharges of the selected watersheds shown in Fig. 1.

We focused our analysis on soluble reactive phosphorus, nitrate, chloride, potassium and alkalinity, in order to consider the most relevant nutrients and some compounds of geochemical interest, but omitting the difficulty of modelling particle transport. Total nitrogen was added later on as it still fitted well into the approach. Fig. 3 shows the time series of loads of these compounds added up for all watersheds for which continuous long-term measurements were available. Only total loads of soluble reactive phosphorus showed a trend that is significantly different from zero over the period of joint availability of data. Note that some stations show small trends in concentrations or loads over certain time periods (see Hari and Zobrist, 2003 and Zobrist et al., 2004 for details). In our approach the export coefficients estimated for these compounds include the effect of transformation processes during transport. Lakes could be of particular importance in this respect, however for the watersheds and sites considered in this study these processes can be assumed to be small (Jakob et al., 1994; Behrendt and Orpitz, 2000). The important effect of water discharge on the loads of the investigated compounds can easily be seen in Fig. 3 by a high correlation of annual loads with annually averaged discharge (loads are high in wet years, low in dry years).

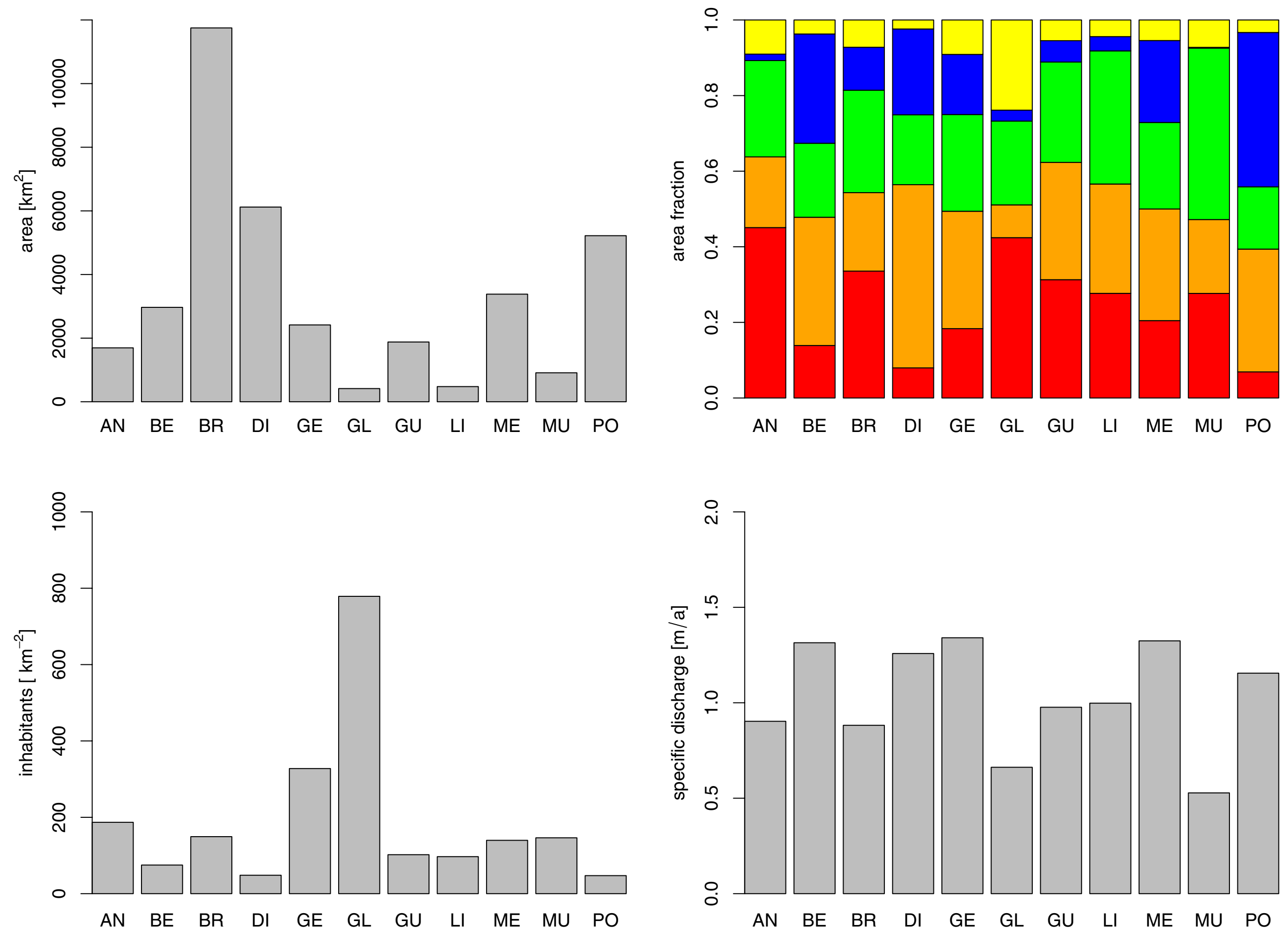


**Figure 2** Watershed areas of the 11 selected measurement sites (top left panel), relative contributions of land use fractions at all sites for the year 1995 (top right panel), number of inhabitants per square kilometre (bottom left panel), and specific discharge (water discharge per area and time) (bottom right panel). Land use fractions in the top right panel are: (i) agriculturally intensively used land (fertilised land) (red), (ii) extensively used land (grass- and bush land, pasture) (orange), (iii) dense forest (green), (iv) barren land (including lakes as a small fraction) (blue), and (v) urban land (settlements and traffic ways) (yellow). Abbreviations of watershed outlet names see legend of Fig. 1.

As consequence, annual loads and water discharge data were averaged over five consecutive years when calculating time-dependent export coefficients to reduce the effect of year-to-year variability but still allow for the identification of trends over decades. Data evaluation was then performed for each of these five-year periods as well as for the complete data set of 24 years (1980—2003).

## Prior knowledge on export coefficients

The Bayesian data analysis approach requires the specification of prior knowledge on model parameters that is independent of the data set used for updating this knowledge. In our study, we gained this knowledge by compiling water quality data of small rivers and springs with watersheds that are dominated by a single land use category and data from studies on agricultural and urban pollutant discharges within Switzerland. Table 2 summarizes mean, standard deviation and number of data points of the data sets for the different compounds and land use categories. Some of these data were extracted from reports of governmental agencies or unpublished data sets. Few nitrate and phosphorus export coefficients were taken from studies addressing pollution from agricultural land (Prasuhn, 1999; Schmid and Prasuhn, 2000; Gächter et al., 2004). Coefficients for chloride, potassium and alkalinity were estimated by multiplying measured concentrations in rivers or springs by the estimated water discharge from watersheds with a single dominating land use. Export coefficients characterizing Swiss urban areas for nutrients could only be found in old studies (Roberts et al., 1976; Dauber et al., 1978). Distributing the total amount of salt used for roads during the winter uniformly over the urban area yields a coefficient in the range of $25 \pm 9$ g Cl m$^{-2}$ a$^{-1}$ with a significant variation from year to year due to differences in winter temperature. The amount of road salt assigned to inhabitants yields $9 \pm 3$ kg inhab$^{-1}$ a$^{-1}$. As these urban areas include settlements and local roads in addition to main roads, it is consistent that a cited value for a highway was even higher (Dauber et al., 1978). Data on specific pollutant loads per capita are derived from Koppe (1999) and Siegrist and Boller (1999). In general, values derived from different data sources show great differences.

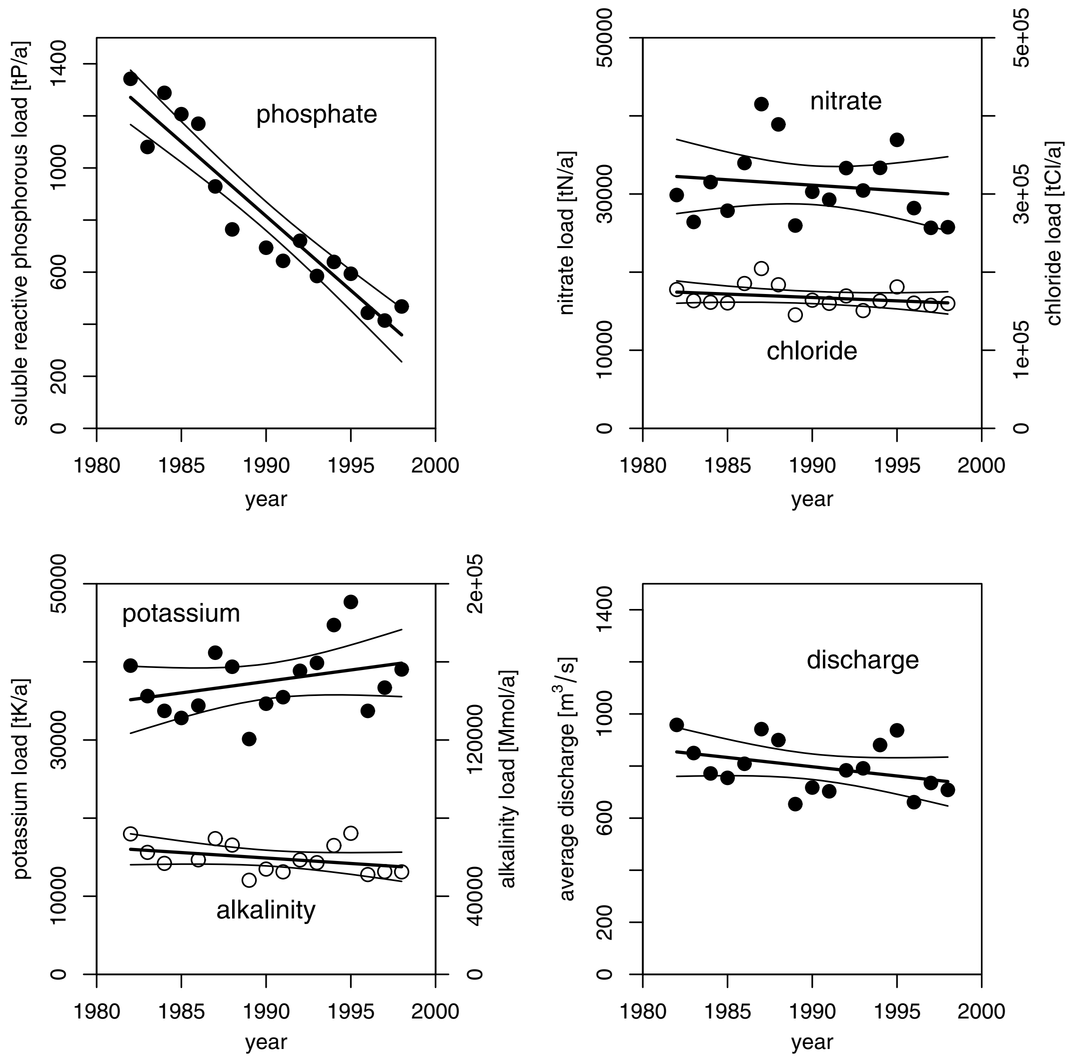


**Figure 3** Total load and water discharge of the watersheds DI, AN, GL, PO and BR as a function of time (the other stations were omitted because they either represent sub-watersheds or do not cover a large fraction of the measurement period). Only soluble reactive phosphorus has a trend over the period of joint data availability that is significantly different from zero.

The measurements summarized in Table 2 indicate that export coefficients for nitrate, soluble reactive phosphorus (SRP) and chloride are significantly higher for intensively used agricultural land compared to extensively used land, forest, or barren land. The high spread of values makes it impossible to identify significant differences within the latter three land use categories. Export coefficients for potassium and alkalinity exhibit a different pattern, since weathering processes contribute significantly to their loads. Data on export coefficients of these substances from urban land are scarce. However, available values are in the same order of magnitude as those for extensively used land, forest and barren land with the exception of chloride. Road salting during the winter is an obvious cause of high contributions from urban areas. The export coefficient characterising phosphorus input from inhabitants decreases strongly between 1980 and 1994 primarily due to a ban of phosphate in household detergents, an increasing fraction of households connected to sewage treatment plants and increased phosphate removal in sewage treatment plants.

Based on an assessment of the data, prior probability distributions of the individual export coefficients were chosen to be lognormal with means and standard deviations given in Table 3. Due to the strong correlation of urban areas with population (not shown), it is clear that our regression approach will not be able to distinguish these two sources. Consequently, urban contributions were assigned to inhabitants by considering the average population density of 2300 persons per km$^2$ of urban area. The differences between the values in Tables 2 and 3 are due to rounding to one significant digit, applying the same value for different land use categories if the difference was felt to be insignificant, and to aggregation of contributions from urban areas and population. All priors were selected to be time-independent in order to search objectively for indication of time dependence in the data. The prior probability density of soluble reactive phosphorus was assigned a very large standard deviation in order to cover the scatter in data as well as the time dependence. The joint prior probability density of each compound for all land use categories consisted of

**Table 2** Arithmetic mean, standard deviation (SD) and number of data points (*n*), of export coefficients calculated from outlet concentrations of small sub-watersheds in the study region that are dominated by a single land use

| Source (land use) | Chemical parameter | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Soluble reactive phosphorus | | | Nitrate | | | Total nitrogen | | | Chloride | | | Potassium | | | Alkalinity | | |
| | $g\ P\ m^{-2}\ a^{-1}$ $kg\ P\ inhab^{-1}\ a^{-1}$ | | | $g\ N\ m^{-2}\ a^{-1}$ $kg\ N\ inhab^{-1}\ a^{-1}$ | | | $g\ N\ m^{-2}\ a^{-1}$ $kg\ N\ inhab^{-1}\ a^{-1}$ | | | $g\ Cl\ m^{-2}\ a^{-1}$ $kg\ Cl\ inhab^{-1}\ a^{-1}$ | | | $g\ K\ m^{-2}\ a^{-1}$ $kg\ K\ inhab^{-1}\ a^{-1}$ | | | $mol\ m^{-2}\ a^{-1}$ $kmol\ inhab^{-1}\ a^{-1}$ | | |
| | Mean | SD | *n* | Mean | SD | *n* | Mean | SD | *n* | Mean | SD | *n* | Mean | SD | *n* | Mean | SD | *n* |
| Agriint | 0.04 | 0.06 | 11 | 3.3 | 1.7 | 13 | 3.8 | 2.5 | 6 | 7.1 | 2.3 | 6 | 0.8 | 0.5 | 5 | 2.8 | 0.8 | 6 |
| Ext | 0.007 | 0.006 | 3 | 0.7 | 0.5 | 4 | 1.0 | – | 1 | 0.8 | 0.4 | 4 | 1.1 | 0.8 | 4 | 3.4 | 0.8 | 4 |
| Forest | 0.007 | 0.005 | 6 | 0.8 | 0.2 | 9 | 0.9 | 0.2 | 3 | 1.1 | 0.6 | 6 | 0.7 | 0.7 | 5 | 1.9 | 0.9 | 6 |
| Barren | 0.005 | 0.002 | 3 | 0.8 | 0.4 | 5 | 1.0 | 0.7 | 2 | 0.9 | 0.1 | 2 | 2.9 | 1.6 | 2 | 1.4 | 0.0 | 2 |
| Urban highway | 0.008 | – | 1 | 1.1 | 0.7 | 5 | 1.7 | 0.8 | 3 | 30 | – | 1 | *0.7* | | | *0.4* | | |
| | | | | | | | | | | 117 | – | 1 | | | | | | |
| Inhab | 0.75 (1980) | – | 1 | 1.8 | 0.1 | | 2.1 | 0.1 | 2 | 4.7 | – | 1 | 1.9 | – | 1 | 0.34 | – | 1 |
| | 0.17 (1994) | 0.06 | 2 | | | | | | | | | | | | | | | |

Abbreviations for land use categories used in the leftmost column are explained in Table 1. Coefficients printed in italics for potassium and alkalinity are best estimates by the authors.

**Table 3** Means and standard deviations (SD) of lognormal prior distributions of the export coefficients

| Source (land use) | Chemical parameter | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Soluble reactive phosphorus | | Nitrate | | Total nitrogen | | Chloride | | Potassium | | Alkalinity | |
| | $g\ P\ m^{-2}\ a^{-1}$ $kg\ P\ inhab^{-1}\ a^{-1}$ | | $g\ N\ m^{-2}\ a^{-1}$ $kg\ N\ inhab^{-1}\ a^{-1}$ | | $g\ N\ m^{-2}\ a^{-1}$ $kg\ N\ inhab^{-1}\ a^{-1}$ | | $g\ Cl\ m^{-2}\ a^{-1}$ $kg\ Cl\ inhab^{-1}\ a^{-1}$ | | $g\ K\ m^{-2}\ a^{-1}$ $kg\ K\ inhab^{-1}\ a^{-1}$ | | $mol\ m^{-2}\ a^{-1}$ $kmol\ inhab^{-1}\ a^{-1}$ | |
| | Mean | SD | Mean | SD | Mean | SD | Mean | SD | Mean | SD | Mean | SD |
| Agriint | 0.04 | 0.06 | 3.0 | 1.5 | 4.0 | 2.0 | 7.0 | 3.5 | 1.0 | 1.0 | 3.0 | 1.5 |
| Ext | 0.007 | 0.007 | 0.8 | 0.4 | 1.0 | 0.5 | 1.0 | 0.75 | 0.8 | 0.8 | 3.0 | 1.5 |
| Forest | 0.007 | 0.007 | 0.8 | 0.4 | 1.0 | 0.5 | 1.0 | 0.75 | 0.8 | 0.8 | 2.0 | 1.0 |
| Barren | 0.007 | 0.007 | 0.8 | 0.4 | 1.0 | 0.5 | 1.0 | 0.75 | 2.0 | 2.0 | 2.0 | 2.0 |
| Inhab | 0.15 | 0.30 | 2.0 | 1.0 | 2.4 | 1.2 | 15 | 15 | 2.0 | 2.0 | 0.32 | 0.24 |

Abbreviations for land use categories used in the leftmost column are explained in Table 1.

**Table 4** Export coefficients obtained by the constrained frequentist parameter estimation procedure (according to Eq. (4)) for the average concentrations and annual loads for the entire period 1980–2003

| Source | Calc. mode | Chemical parameter | | | | | |
|---|---|---|---|---|---|---|---|
| | | Soluble reactive phosphorus | Nitrate | Total nitrogen | Chloride | Potassium | Alkalinity |
| | | g P $m^{-2}$ $a^{-1}$ kg P $inhab^{-1}$ $a^{-1}$ | g N $m^{-2}$ $a^{-1}$ kg N $inhab^{-1}$ $a^{-1}$ | g N $m^{-2}$ $a^{-1}$ kg N $inhab^{-1}$ $a^{-1}$ | g Cl $m^{-2}$ $a^{-1}$ kg Cl $inhab^{-1}$ $a^{-1}$ | g K $m^{-2}$ $a^{-1}$ kg K $inhab^{-1}$ $a^{-1}$ | mol $m^{-2}$ $a^{-1}$ kmol $inhab^{-1}$ $a^{-1}$ |
| | | Estimate | Estimate | Estimate | Estimate | Estimate | Estimate |
| Agriint | C | 0.069 | 3.8 | 5.1 | 10 | 3.1 | 5.4 |
| | L | 0.031 | 3.1 | 3.5 | 12 | 2.2 | 3.4 |
| Ext | C | 0 | 0.17 | 1.2 | 0 | 0.28 | 4.4 |
| | L | 0 | 0.45 | 1.0 | 0 | 0.38 | 3.8 |
| Forest | C | 0 | 0.071 | 0 | 0 | 0 | 0 |
| | L | 0 | 0 | 0 | 0 | 0 | 0 |
| Barren | C | 0 | 0.43 | 0.34 | 9.1 | 2.8 | 0.68 |
| | L | 0 | 0.35 | 0.70 | 11 | 2.7 | 0 |
| Inhab | C | 0.17 | 2.1 | 2.0 | 19 | 1.9 | 0.023 |
| | L | 0.18 | 2.3 | 3.3 | 13 | 3.0 | 4.2 |

Abbreviations for land use categories used in the leftmost column are explained in Table 1. ''C'' indicates estimation from concentration data, ''L'' from load data.

the product of the marginal densities for the different land uses (assumption of independence of prior knowledge between different land uses).

## Results

Parameter estimations were performed using average annual loads (according to Eq. (1)) and average concentrations (according to Eq. (2)) at the watershed outlets for all five-year sub-periods of the investigation period from 1980 to 2003 and for the entire period. In the following sub-sections, we present estimated values of export coefficients (section 'Export coefficients'), implications for concentration and load contributions by different source categories (section 'Contribution of source categories to concentrations and loads') and estimation of background concentrations in the absence of anthropogenic impairment (section 'Estimation of background concentrations').

### Export coefficients

The results for export coefficients based on average concentrations and loads over the entire period are summarized in Tables 4 and 5 for the frequentist and for the Bayesian estimation, respectively. These results are interpreted by chemical compound in the following sub-sections together with some results on the time series of export coefficients.

#### Phosphorus

Fig. 4 shows the results of the estimation of export coefficients based on SRP concentrations for all 21 (overlapping) five-year periods from 1980–1984 to 2000–2003. A comparison of the estimates of the means and the 10th and 90th percentiles of the Bayesian prior and posterior distributions indicates that we cannot gain information on the small per area contributions from extensively used land, forest, and barren land from concentrations at the watershed outlets (the marginal posterior distributions are not significantly narrower than the priors). However, we get an improved estimate of the per area contribution from intensively used agricultural land and can constrain the contribution per inhabitant considerably. The contribution per inhabitant decreases from 1980 to 1990 from about 0.5 kg P $inhab^{-1}$ $a^{-1}$ to about 0.04 kg P $inhab^{-1}$ $a^{-1}$. This is primarily a consequence of the ban of phosphate in household detergents in 1986 (Siegrist and Boller, 1999). Our analysis demonstrates that this measure had a very strong effect on phosphate concentrations in Swiss rivers. There may also be a contribution to this effect by increased phosphorus elimination rates due to the connection of households to sewage treatment plants and improved plant performance. The contribution from intensive agriculture indicates a slight rise from 1980 to 1990 and a slight decrease from 1990 to 2003. This could indicate intensification of agricultural practices during the first half of the investigation period and an effect of reduced fertilizer application, decreased animal density and improved phosphate retention in the second half. However, the uncertainty of the export coefficient estimates is too large to identify this trend significantly. The frequentist technique, which ignores prior knowledge, shows the same general trends. However, it is not able to identify the small contributions from extensively used land, forest, and barren land (it sets these contributions to zero and compensates for this by increasing the contribution from intensively used agricultural land). These difficulties of the frequentist approach are not surprising, as the marginal Bayesian posterior is not significantly different from the prior for these export coefficients.

**Table 5** Means and standard deviations (SD) of export coefficients obtained by the Bayesian parameter estimation procedure (according to Eq. (5)) for the average concentrations and annual loads for the entire period 1980–2003

| Source | Calc. mode | Chemical parameter | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Soluble reactive phosphorus | | Nitrate | | Total nitrogen | | Chloride | | Potassium | | Alkalinity | |
| | | $g\ P\ m^{-2}\ a^{-1}$<br>$kg\ P\ inhab^{-1}\ a^{-1}$ | | $g\ N\ m^{-2}\ a^{-1}$<br>$kg\ N\ inhab^{-1}\ a^{-1}$ | | $g\ N\ m^{-2}\ a^{-1}$<br>$kg\ N\ inhab^{-1}\ a^{-1}$ | | $g\ Cl\ m^{-2}\ a^{-1}$<br>$kg\ Cl\ inhab^{-1}\ a^{-1}$ | | $g\ K\ m^{-2}\ a^{-1}$<br>$kg\ K\ inhab^{-1}\ a^{-1}$ | | $mol\ m^{-2}\ a^{-1}$<br>$kmol\ inhab^{-1}\ a^{-1}$ | |
| | | Mean | SD | Mean | SD | Mean | SD | Mean | SD | Mean | SD | Mean | SD |
| Agriint | C | 0.043 | 0.035 | 2.98 | 0.68 | 4.29 | 0.84 | 8.32 | 3.04 | 1.92 | 1.00 | 3.86 | 1.08 |
| | L | 0.029 | 0.019 | 2.91 | 0.22 | 3.25 | 0.42 | 9.14 | 3.48 | 1.81 | 0.47 | 3.73 | 0.72 |
| Ext | C | 0.0061 | 0.0052 | 0.56 | 0.31 | 0.83 | 0.35 | 1.02 | 0.71 | 0.66 | 0.50 | 3.08 | 1.01 |
| | L | 0.0041 | 0.0031 | 0.36 | 0.09 | 0.78 | 0.21 | 1.29 | 0.90 | 0.38 | 0.19 | 2.85 | 0.60 |
| Forest | C | 0.0066 | 0.0059 | 0.59 | 0.31 | 0.80 | 0.37 | 1.00 | 0.76 | 0.54 | 0.48 | 1.70 | 0.78 |
| | L | 0.0056 | 0.0044 | 0.48 | 0.18 | 0.87 | 0.35 | 1.20 | 0.96 | 0.72 | 0.57 | 2.07 | 0.89 |
| Barren | C | 0.0065 | 0.0059 | 0.61 | 0.31 | 0.88 | 0.38 | 1.14 | 0.85 | 2.05 | 0.99 | 1.84 | 0.77 |
| | L | 0.0044 | 0.0033 | 0.39 | 0.11 | 0.76 | 0.24 | 1.97 | 1.90 | 2.40 | 0.32 | 1.36 | 0.52 |
| Inhab | C | 0.16 | 0.05 | 2.16 | 0.51 | 2.18 | 0.58 | 18.9 | 4.2 | 2.21 | 0.81 | 0.32 | 0.22 |
| | L | 0.16 | 0.04 | 2.02 | 0.41 | 2.70 | 0.75 | 21.8 | 7.9 | 2.85 | 0.73 | 0.39 | 0.13 |

Abbreviations see Table 4.

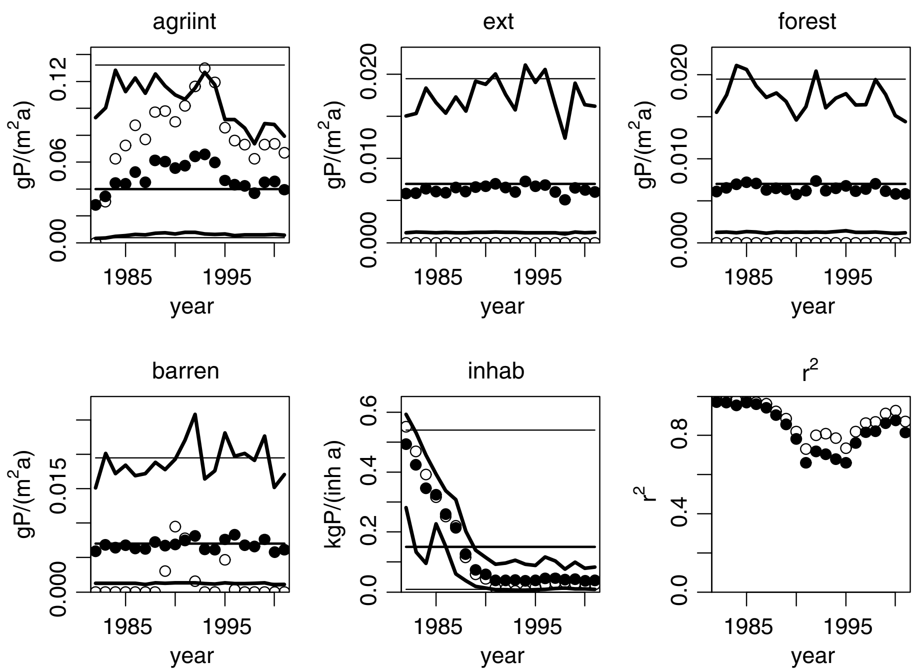


**Figure 4** Export coefficients estimated by the frequentist and Bayesian analyses of soluble reactive phosphorus concentrations (panels 1—5) and the value of $r^2$ for the frequentist estimates and mean of the Bayesian estimates (panel 6). Open circles represent the frequentist estimates, solid circles the means of the Bayesian posterior distributions. Thick varying lines indicate 10th and 90th percentiles of the Bayesian posterior distribution. The horizontal lines indicate the means and the 10th and 90th percentiles of the prior distributions. Results on the *y*-axis are plotted at the means of the five-year periods on the *x*-axis.

The results for the average concentrations and loads of all investigated years (Table 5) confirm the dominance of intensively used agricultural land on phosphate export per area. The export coefficients for extensively used land, forest and urban land are in the order of the atmospheric deposition rates of 0.005—0.01 g P $m^{-2}$ $a^{-1}$. If we neglect erosion of particulate phosphorus, this good correspondence indicates negligible net loss of phosphorus from these land use categories. On the other hand, the significantly higher value of the export coefficient for intensively used agricultural land reflects the effect of fertilization. For this land use category, loss of phosphorus in particulate form by erosion may also be an important component of the total phosphorus mass balance.

The data for total phosphorus (not shown) did not lead to a reasonable fit of the model. The major reason for this is that the model used in this study is too simple to account for processes involving particulate substances (e.g. intensity of rain, storm events, sedimentation in lakes are all relevant influence factors for loss and transport of particles and are not addressed in this simple model). More complex watershed models, as cited in the introduction, are required to analyze the behaviour of particulate substances.

## Nitrogen

Fig. 5 shows the results of the estimation of export coefficients based on nitrate concentrations for all 21 (overlapping) five-year periods from 1980—1984 to 2000—2003. Due to the uncertainty in export coefficient estimates, the slight decrease in the contribution from inhabitants over the investigation period is not significant. Estimates of export coefficients based on nitrate loads (not shown) show a small decrease in the coefficient from intensively used agricultural land at the end of the investigation period, instead. Therefore, the small reduction in nitrate loads or concentrations cannot uniquely be attributed by our simple model to an increasing number of denitrifying sewage treatment plants or to measures taken in agriculture.

Apart from this minor trend, the coefficients for average loads and concentrations of the entire investigation period given in Table 5 represent the results of the analysis quite well. It is evident that intensively used agricultural land has by far the highest per area contribution of all land use categories.

The results for total nitrogen (not shown graphically) are similar to those for nitrate because nitrate is the dominating component of total nitrogen (from 55% for alpine rivers to 90% for rivers on the Swiss plateau). If contributions by particulate nitrogen would be more important, the results of our simple model for total nitrogen would probably be poor for the same reasons as for total phosphorus.

The total nitrogen export coefficients for extensively used land, barren land and forests are significantly below the atmospheric deposition rate of about 0.76 g N $m^{-2}$ $a^{-1}$ for oxidised nitrogen plus 1.22 g N $m^{-2}$ $a^{-1}$ for reduced nitrogen (EMEP, 2000). This decrease is likely caused by denitrification in soils and in lake sediments to a smaller extent.

## Chloride

The estimated export coefficients for chloride do not show any significant trend over the investigation period (not shown). The frequentist approach (results for the entire investigation period given in Table 4) fails to estimate per

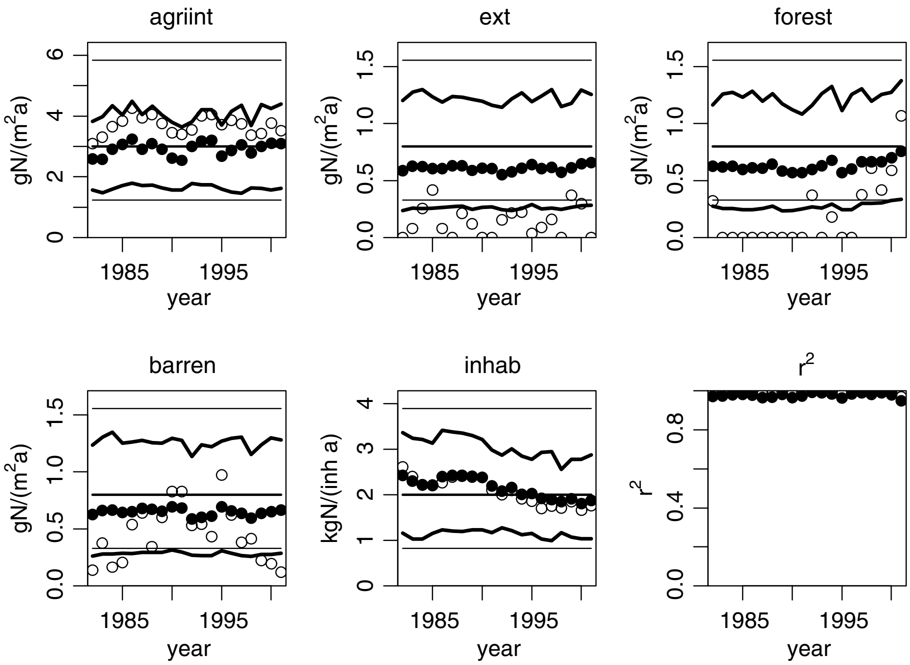


**Figure 5** Export coefficients estimated by the frequentist and Bayesian analyses of nitrate concentrations (panels 1—5) and the value of $r^2$ for the frequentist estimates and mean of the Bayesian estimates (panel 6). For symbols used see Fig. 4.

area contributions from extensively used land and forests, and it overestimates the contribution from barren land (compared to our prior knowledge). The Bayesian approach (results for the entire investigation period given in Table 5) demonstrates that intensive agriculture is the dominating per area contribution to chloride concentration in the river. Inhabitants provide chloride by point sources as well as by road salting (this was considered in our assessment of prior estimates given in Table 3).

Export coefficients for chloride exceed the wet atmospheric deposition rate of 0.2—0.3 g Cl $m^{-2}$ $a^{-1}$ in rural areas of Switzerland (BUWAL, 2000a,b). This indicates an influence of the deposition of chloride containing aerosols. Deposition rates in urban areas are in the order or 1.3 g Cl $m^{-2}$ $a^{-1}$ (Zobrist et al., 1993).

**Potassium**

The estimated export coefficients for potassium do not show any significant trend over the investigation period (not shown). The export coefficients for potassium (results for the entire investigation period given in Table 5) depend much less on land use categories than those for phosphate and nitrate. This result is due to the dominant source of potassium by weathering processes. Weathering of silicate rock and clay minerals probably causes the high value for barren land without elimination by plant harvesting. Fertilization explains the higher value for intensively used agricultural land in contrast to extensively used land and forests.

Estimated export coefficients for potassium exceed by far the total atmospheric deposition rates of potassium of 0.13 g K $m^{-2}$ $a^{-1}$ (Zobrist et al., 1993). This is a consequence of weathering and fertilization.

**Alkalinity**

The estimated export coefficients for alkalinity do not show any significant trend over the investigation period (not shown). A comparison of the posterior estimates for the entire period from Table 6 with the priors given in Table 4 shows that we cannot learn much from the alkalinity data (the posterior distributions are only slightly narrower than the prior). The decrease of the export coefficients going down from intensively used agricultural land to extensively used land to forest and barren land reflects the dependence of weathering of calcareous rocks on temperature and elevation (Drever and Zobrist, 1992). Limestone weathering is

**Table 6** Means and ranges of estimated background concentrations for all watersheds

| Chemical parameter | Unit | Arithmetic mean | Minimum | Maximum |
|---|---|---|---|---|
| Soluble reactive phosphorus | g P $m^{-3}$ | 0.005 | 0.003 | 0.011 |
| Nitrate | g N $m^{-3}$ | 0.5 | 0.3 | 1.1 |
| Total nitrogen | g N $m^{-3}$ | 0.8 | 0.5 | 1.5 |
| Chloride | g Cl $m^{-3}$ | 1.1 | 0.7 | 2.3 |
| Potassium | g K $m^{-3}$ | 0.8 | 0.5 | 1.4 |
| Alkalinity | mol $m^{-3}$ | 2.3 | 1.5 | 4.5 |

regulating the water composition of all rivers included in this study (Zobrist et al., 2004). Carbon dioxide, which dissolves calcareous rock in the underground, is produced by microbial activities in soils. Therefore, the highest production of alkalinity occurs on low elevation land with the highest microbial activity in soil, i.e. on intensively used agricultural land. In contrast, on barren land, usually situated at high elevation and in a colder environment, $CO_2$ production is small.

As the estimated export coefficients in Table 5 show, weathering of calcareous rocks completely neutralise the atmospheric input of strong acids in the range of 0.005–0.05 mol $m^{-2}$ $a^{-1}$ (Zobrist et al., 1993) as well as the strong acid produced by the nitrification of the deposited ammonium.

## Contributions of source categories to concentrations and loads

When multiplying the export coefficients (Table 5) by the areas of the land use categories of each watershed (Fig. 2) and dividing by the corresponding discharge, we obtain the contributions of different land uses to the total concentration at the watershed outlets (see Eq. (2)). This is of interest to identify dominating sources of the investigated compounds for each watershed.

### Phosphorus

Fig. 6 shows the results of such an analysis for SRP concentrations for the first (1980–1984) and the last (1999–2003) five-year period within the investigation time frame. The fit of the model is quite good with the exception of the Thur River at Andelfingen (AN) in the more recent period where it is considerably underestimated by the model. This may be caused by a greater than average intensity of animal farming in this watershed. When comparing the results of the two time periods shown in Fig. 6, it becomes evident that the concentrations decreased considerably over time (note the difference in scale). As already discussed, this is a consequence of the ban of phosphate in household detergents in 1986, the increasing fraction of households connected to wastewater treatment plants, and the improved performance of wastewater treatment plants. These measures resulted in a shift of the dominating source from point sources to diffuse sources as is clearly shown in Fig. 6. In many watersheds, intensively used agricultural land is now the major source of phosphate in the river.

### Other compounds

As time dependence of export coefficients of the other investigated compounds is minor and statistically not significant we show only the results for the export coefficients based on river concentrations averaged over the whole investigation period (Fig. 7). The fit of the model to the data of these compounds is even better than the fit for phosphate (Fig. 6).

For most rivers, except for the alpine watersheds of the Rhine River at Diepoldsau (DI) and the Rhone River at Porte-du-Scex (PO), intensive agriculture is an important or even the dominating source of nitrate. Contributions by point sources are only dominant for the Glatt River at Rheinsfelden (GL), which drains a watershed that is extremely densely populated (see Fig. 2). Point sources are also relevant in some other watersheds. All the other contributions to nitrate concentrations at watershed outlets are small.

The poor fit of the measured chloride concentration of the Rhone river at Porte-du-Scex (PO) is caused by industrial inputs that do not occur at a similar amount as the other watersheds (and are therefore not considered in our model). Chloride concentrations are dominated by human influences, represented by the contribution proportional to inhabitants. This includes point sources and diffuse sources from urban areas, in this case mainly the contribution from road salting (see section ''Prior knowledge on export coefficients'').

The relative contributions to potassium concentrations in the watershed outlets are very similar to the relative nitrate contributions with the exception of the higher relative

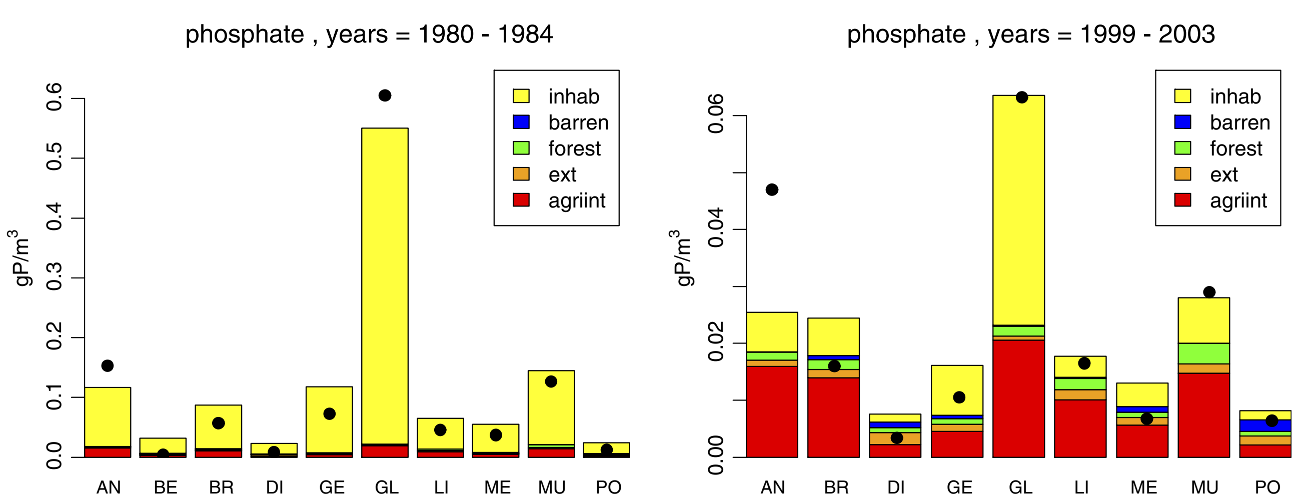


**Figure 6** Calculated contributions of land use categories to the concentration of soluble reactive phosphorus (SRP) at river stations used in the analysis (bar diagrams), and measured concentrations averaged over the same time period (black, filled circles). Results are shown for mean export coefficients of the Bayesian analysis for SRP concentrations. First five year period, 1980–1984 (left), and last five year period, 1999–2003 (right). Note the difference in scale. For abbreviations of station names see Table 2.

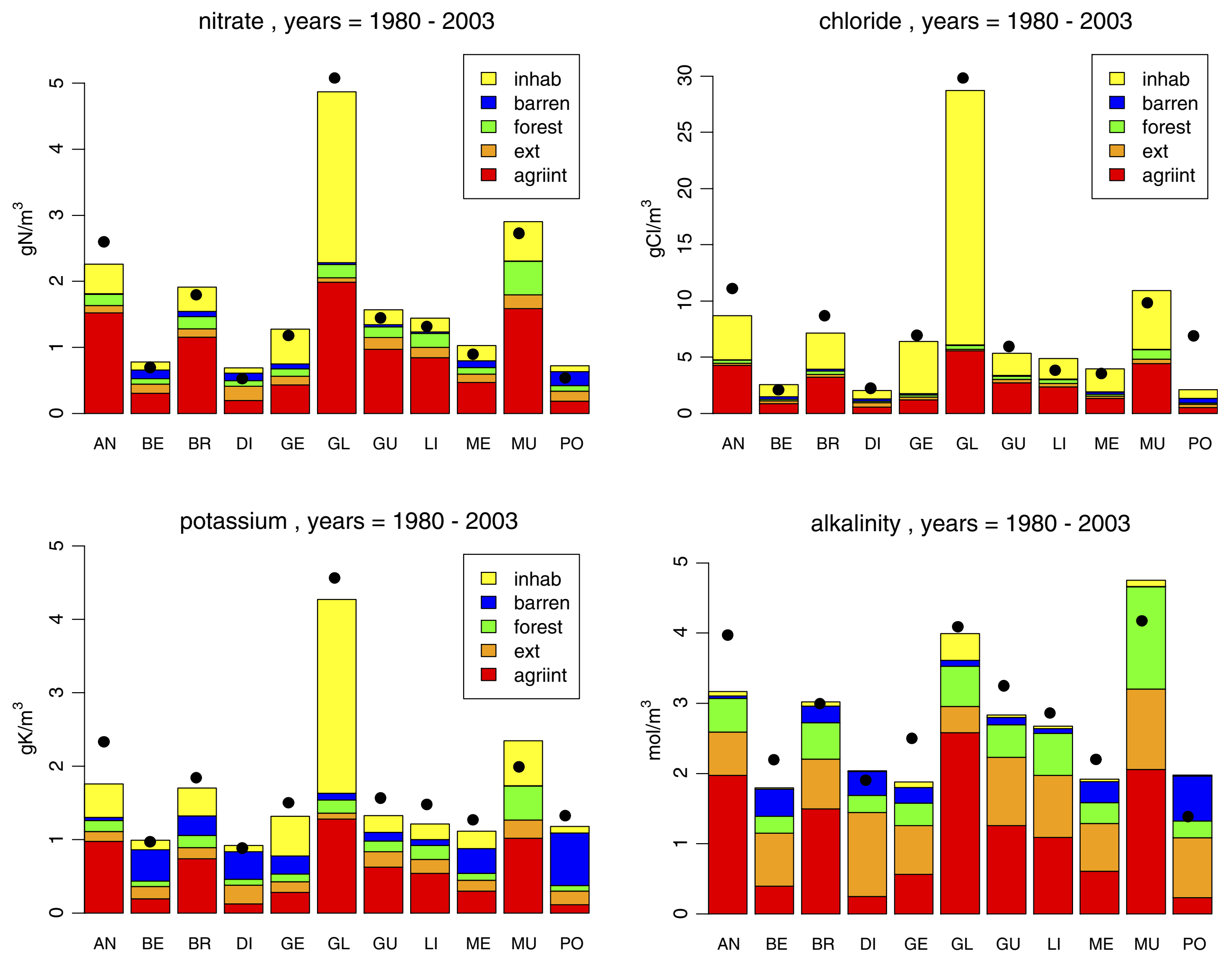


**Figure 7** Calculated contributions of land use categories to the concentrations of nitrate, chloride, potassium, and alkalinity at river stations used in the analysis (bar diagrams), and measured concentrations averaged over the complete investigation period (black, filled circles). For abbreviations of station names see Fig. 2.

contribution by barren areas. This indicates similar sources with the exception of weathering processes, which explain the higher relative contribution of barren areas to potassium.

Alkalinity shows a quite different distribution pattern than the other chemical parameters. Inhabitants contribute only very little to the observed alkalinity concentrations at watershed outlets. The relative contributions of alkalinity correspond quite well to the land use fractions, as the export coefficients vary much less with land use than in the case of the other compounds (see Table 5). A more significant effect due to variations in rock composition and different average elevations of watersheds may cause the higher deviations of model results from measurements than for the other compounds.

## Estimation of background concentrations

The export coefficients estimated in section ''Contributions of source categories to concentrations and loads'' allow us to estimate background concentrations in rivers in the absence of anthropogenic impairment due to point sources and leaching from intensively used agricultural land. These background concentrations can be calculated by summing up the contributions from different land uses as in the preceding section but with omission of the contribution by inhabitants and by replacing the export coefficient for intensively used agricultural land by the coefficient for extensively used land. The background concentrations estimated by this procedure still contain the contributions by the anthropogenically increased atmospheric input as this contribution is contained in all estimated export coefficients. Background concentrations were calculated for all watersheds (Table 6) using the estimated export coefficients based on concentration and load data (Table 5).

These background concentrations depend on the specific water discharge (see Fig. 2) since the model assumes a constant load for each land use category. Due to the important contributions by inhabitants and intensive agriculture (see section ''Estimation of background concentrations''), the background concentrations are much smaller than the actual concentrations at the investigated measurement sites for all substances with exception of alkalinity. However, they are in a similar order of magnitude as concentrations measured in rivers and groundwater in Switzerland that are not impaired by anthropogenic inputs.

## Discussion

There are three factors that make it difficult to uniquely identify export coefficients with frequentist techniques from the available watershed data alone:

- the simplicity of the model can only lead to a description of the major trends and orders of magnitude of the contributions of different sources to water pollution. It can be expected that due to many factors not considered in the model, significant variability will remain in the residuals.
- for most substances there will be a small number of dominating source categories while other categories contribute only by a small amount to loads and concentrations in the rivers. This makes these small contributions hard to identify.
- some of the land use fractions (especially extensively used land and forest) do not vary strongly from one watershed to the other (see Fig. 2). This leads to poor conditioning of the regression problem and enhances the problem of identifying small contributions to total loads or concentrations.

The occurrence of these problems led to (i) negative estimates of some (usually small) export coefficients when performing unconstrained maximization in Eq. (4), (ii) the occasional occurrence of jumps in time series of export coefficients (e.g. switching the major contribution from one source category to the other), (iii) the occasional occurrence of significant deviations of export coefficient estimates from prior knowledge (summarized in Table 2), and (iv) poor results of regression diagnostics. These problems demonstrate that it is difficult to infer by the frequentistic technique contributions of source categories from observed concentrations or loads in rivers only. In most cases only small load or concentration contributions caused the identifiability problems whereas the major contributions could be identified when neglecting the small contributions.

As prior knowledge of export coefficients is available (see section ''Prior knowledge on export coefficients'') it can be used to overcome the identifiability problem by combining prior knowledge with river survey data to get the best possible estimate of export coefficients for the investigated watersheds. Bayesian inference provides the ideal conceptual basis for such an analysis. It makes it possible to estimate all parameters jointly even in the case of poor identifiability. The property of the priors of being zero for negative concentrations naturally excludes negative solutions, and a comparison of posterior with prior distributions make an assessment of identifiability possible (in cases of very poor identifiability, the posterior distribution is nearly equal to the prior).

Our results demonstrate that the conceptual advantages of the Bayesian approach (under poor identifiability and availability of prior knowledge) can be realized. It leads to reasonable estimates of all export coefficients and all land use categories. The scatter between predicted total concentrations (sum of contributions by all land use types) and measured concentrations are astonishingly small for such a simple model (see Figs. 6 and 7). This makes this model to a cheap analysis tool of long-term trends in export of the investigated compounds from different land uses. In addition, once the coefficients have been estimated, they can be used as an estimator of the effects of land use change or of loads in ungauged watersheds.

In principle, further improvement to the model may be possible by considering more external influence factors (such as precipitation or specific river discharge) or by parameterizing more processes in the watershed (e.g. consider the effect of lakes, different soil types or more land use categories). However, we think that there are not much possibilities for improvement because it may be realistic to assume that remaining heterogeneity of watershed properties and land use management may be the major source for the scatter between calculated and measured concentrations or loads.

## Summary and conclusions

By combining prior knowledge of export coefficients with data from 11 watershed outlets in Switzerland we estimated export coefficients for phosphate, nitrate, total nitrogen, chloride, potassium and alkalinity from different land use categories over a 24 year investigation period. The results show clearly that there was a drastic reduction in point source contributions of phosphate to Swiss rivers between 1980 and 1990. This reflects measures taken to reduce phosphate discharge into receiving water bodies. The most significant contributions to this reduction are caused by the ban of phosphate in household detergents, the increasing fraction of households connected to sewage treatment plants and improvement of phosphate removal in sewage treatment plants. There was no significant trend in any of the other loads or export coefficients. This indicates that other measures (control of fertilizer application, buffer strips and avoiding fallow lands) taken to prevent transfer of these substances to receiving waters, have not (yet) shown a sufficiently high effect to be detected by our model.

Application of the simple export coefficient-based model to the whole country of Switzerland demonstrates that for SRP, nitrate, total nitrogen, chloride and potassium, contributions by point sources (and road salting) and from intensive agriculture by far dominate the loads from forests, extensively used land and barren land. This implies that the background concentrations of these substances in the absence of increased discharges due to human activities would be much smaller.

Due to the poor conditioning of the regression problem, frequentist parameter estimation techniques fail to give reasonable results. It is demonstrated that the combination of prior knowledge about export coefficients with measured data leads to significantly better results. Bayesian data analysis is shown to be an ideal mathematical framework to support this type of work. This methodology is relatively easy to apply and leads to results that can be used to get coarse estimates of the loads of the investigated compounds from ungauged watersheds with similar climatic, topographic and soil conditions, similar land management in intensively used agricultural areas and similar wastewater treatment technology and industrialization. Furthermore, it can be used to derive estimates of the consequences of land use change to river water quality. The present study can be expected to lead to more accurate estimates of export coefficients compared to earlier studies because of the flow proportional sampling procedure, which gives excellent load data. Furthermore, we included chloride, potassium and alkalinity data in an analysis that has primarily been applied to nutrients in the past.

To improve our capability of interpreting watershed outlet loads, it would be beneficial to: (i) perform similar studies in watersheds of different characteristics, (ii) analyse the dependence of estimated export coefficients on external influence factors (such as precipitation, soil type, average slope, agricultural management practices, temperature), and (iii) use this information to include the most important external influence factors in an extended version of the model. Such a model is useful to complement more detailed mechanistic watershed modelling and to support the difficult calibration process of such models (Abbaspour et al., 2006).

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