Hydrol. Earth Syst. Sci. Discuss., 8, 7555–7594, 2011
www.hydrol-earth-syst-sci-discuss.net/8/7555/2011/
doi:10.5194/hessd-8-7555-2011

Hydrology and Earth System Sciences Discussions

Modelling nitrogen and phosphorus loads in a Mediterranean river catchment (La Tordera, NE Spain)

F. Caille[1], J. L. Riera[2], and A. Rosell-Melé[1,3]

[1]Institute of Environmental Science and Technology (ICTA), Autonomous University of Barcelona (UAB), Bellaterra 08193, Spain
[2]Department of Ecology, University of Barcelona (UB), Diagonal 645, Barcelona 08028, Spain
[3]Institució Catalana de Recera i Estudis Avançats, Pg. Lluís Companys 23, 08010 Barcelona, Spain

Received: 18 July 2011 – Accepted: 22 July 2011 – Published: 2 August 2011

Correspondence to: F. Caille (frederique.caille@gmail.com)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Human activities have resulted in increased nutrient levels in many rivers all over Europe. Sustainable management of river basins demands an assessment of the causes and consequences of human alteration of nutrient flows, together with an evaluation of management options. In the context of an integrated and interdisciplinary environmental assessment (IEA) of nutrient flows, we present and discuss the application of the nutrient emission model MONERIS (MOdelling Nutrient Emissions into River Systems) to the Catalan river basin, La Tordera (North-East of Spain), for the period 1996-2002. After a successful calibration and verification process (Nash-Sutcliffe efficiencies $E = 0.85$ for phosphorus, and $E = 0.86$ for nitrogen), the application of the model MONERIS proved to be useful to estimate nutrient loads. Crucial for model calibration, in-stream retention (mainly affected by variability in precipitation) was estimated to be about 50 % of nutrient emissions on an annual basis. Through this process, we identified the importance of point sources for phosphorus emissions (about 94 % for 1996–2002), and diffuse sources, especially inputs via groundwater, for nitrogen emissions (about 31 % for 1996–2002). Despite potential hurdles related to model structure, observed loads, and input data encountered during the modelling process, MONERIS provided a good representation of the major interannual and spatial patterns in nutrient emissions. An analysis of the model uncertainty and sensitivity to input data indicates that the model MONERIS, even in data-starved Mediterranean catchments, may be profitably used for evaluating quantitative nutrient emission scenarios that may help catchment managers and planners to develop effective policy and management measures to reduce nutrient loads.

1 Introduction

The water quality of rivers in developed countries, and in particular in Europe, has improved significantly over the last few decades thanks both to current EU and national legislation and enforcement, and to changes in social attitudes towards the environment (EEA, 1999; EEA, 2003). Nonetheless, nutrient emissions are still a key environmental issue in fresh and coastal waters (Vitousek et al., 1997). In this context, the European Water Framework Directive (WFD, Directive 2000/60/EC) has been designed to achieve good ecological and chemical status for all European water bodies by 2015 (WFD, 2002), promoting a new approach to water and land management through river basin planning. One of the aims of the WFD is to reduce the impacts of eutrophication caused by excess nutrient inputs through point and diffuse pollution from urban and rural areas. To assess whether this objective of the WFD can be achieved, modelling of nutrient fluxes under plausible future scenarios is necessary. This requires an understanding and analysis of past and present nutrient sources, magnitudes of inputs and distribution of loads within subcatchments.

Models are useful assessment tools for the quantification of pollution pressures by nutrients (De Wit, 2000). Over the last decade, many different models of nutrient transport, retention and loss in river basins have been developed within European countries (Kronvang et al., 1995; Arheimer and Brandt, 1998; Behrendt et al., 2000). Conceptual, physically-based process models have been developed to describe pollutant mobilisation, transport and retention in soils, groundwater and surface waters (Conan et al., 2003; Billen and Garnier, 2000; Arnold et al., 1998; Whitehead et al., 1998). Other simpler, empirical catchment models have been based on the export-coefficient approach (Hetling et al., 1999), GIS-based mass balance method (Pieterse et al., 2003) and statistical regressions (Seitzinger et al., 2002; Behrendt and Optiz, 2000). Each model was initially developed for a different region and goal, and differed from other models in its complexity, spatial and temporal resolution, and data requirements. The selection of an appropriate model for a particular application must be made attending to these characteristics, and will always be limited by data availability. In general terms, a model needs to be functional with respect to scale (Addiscott, 1993), with a degree of complexity that will depend on the area of the catchment to be modelled, with simpler models generally applied to larger catchments (Addiscott and Mirza, 1998; Whitmore et al., 1992).

HESSD
8, 7555–7594, 2011

Among the large number of models available for assessing nutrient loads, MONERIS (MOdelling Nutrient Emissions in RIver Systems) is a steady-state, conceptual, lumped-parameter model that has been widely used, especially in northern and central Europe, to estimate annual nitrogen (N) and phosphorus (P) loads (Behrendt and Opitz, 2000; Behrendt et al., 2000; Behrendt et al., 2007). MONERIS also provides estimates of emissions through different point and diffuse pathways, and estimates of retention in the stream network. MONERIS is appropriate for estimating the point and diffuse sources of nutrients in data-sparse catchments where high temporal resolution, dynamic models would be difficult or impossible to apply, and whenever a relatively rapid assessment of the main nutrient emission pathways is needed. These conditions are typical of many real-life management situations in Mediterranean countries. To make the application of the model reliable and effective, model calibration must be followed by an analysis of uncertainties and sensitivity. Appraisal of the sources of uncertainty is necessary to evaluate the reliability of the model, while an assessment of model sensitivity is required to determine the model response to changes in driving factors, in particular land use change and management scenarios.

In the context of an integrated environmental assessment of a Mediterranean river catchment (Caille et al., 2009) we present an application of the model MONERIS to the estimation and apportionment of nitrogen and phosphorus emissions to the Catalan river La Tordera (NE Spain) for the 1996–2002 period, which corresponds to the implementation of the main waste water treatment plants in this catchment. La Tordera exemplifies the consequences of increasing population, urbanisation, tourism, agriculture and industrial activity on nitrogen and phosphorus loads on the catchment waterways. Here, the chief objective is to validate the application of MONERIS to La Tordera catchment in order to explore future scenarios in the context of river basin management plans (Caille et al., 2007), as required by the European WFD. For this purpose we undertook a compilation of data on direct and diffuse nutrient emissions for the period 1996–2002, and used these to calibrate and verify the estimated nutrient loads using MONERIS, over time and across subcatchments. We also assessed sources of

HESSD
8, 7555–7594, 2011

uncertainty in the model, and evaluated model sensitivity.

2 Study area

The Tordera basin (877 km^2) is located in Catalonia (NE Spain), about 60 km north-east of Barcelona. La Tordera stream originates in the Montseny massif (maximum altitude, 1712 m a.s.l.), and runs for about 60 km along the valley formed by this massif and the coastal mountain range of Montnegre before ending in a delta between two important tourist towns, Malgrat de Mar and Blanes (Fig. 1).

The catchment geology is composed mainly of solid, poor porosity plutonic and metamorphic rocks overlaid by sandy, unconsolidated quaternary deposits forming wide terraces and a significant fluvial aquifer in the mid and lower sections of the river.

The climate is sub-humid Mediterranean. Mean temperature ranged from 5 to 10 °C in winter (November–March) and from 20 to 25 °C in summer (July–September); mean annual precipitation was 780 mm yr^{-1} over the 1996–2002 period, with large variations both temporally and spatially (Fig. 2). The hydrologic regime of the streams follows the climatological patterns, with low or intermittent flows during summer and higher, permanent flows from late autumn to early spring. River flow was also highly variable among years. For example, at the Fogars gauging station, 10 km upstream the mouth of La Tordera, median discharge from 1994 to 2003 was 0.95 m^3 s^{-1}, with a range from 0 to 170 m^3 s^{-1}.

The catchment spreads over 25 municipalities in three counties (La Selva, El Vallès Oriental and El Maresme), and includes sections of two Natural Parks: Montseny and Montnegre-Corredor. The main land uses are forests and grassland (77 %), covering most of the mountainous terrain, agricultural lands (16 %), mostly on the low elevation north-eastern part of the catchment, and urban and industrial lands (7 %), mostly along the main valley (Fig. 1).

The population of La Tordera catchment has nearly doubled over the last thirty years, increasing from 59 000 inhabitants in 1975 to 65 000 in 1985, 76 000 in 1995 and

HESSD
8, 7555–7594, 2011

103 000 in 2005 (census data from IDESCAT, http://www.idescat.cat). This trend reflects changes in human activities in the catchment, which have increased during the 1990s. Indeed, the spatial relocation of industrial companies and the improvement of leisure and residential areas in Barcelona and its surroundings, including La Tordera catchment, led to a territorial change, i.e., the transformation of agricultural lands into urban and tourist uses, that is a general trend in developed countries (Soja, 2000; Luzón et al., 2003).

Today, the agency in charge of managing La Tordera is the Catalan Water Agency (Agència Catalana de l'Aigua, ACA). This public organisation is the only water administration of the Catalan Government with full authority on the internal catchments of Catalonia. From the end of the 1990s, as required by the Urban Waste Treatment Directive (UWWTD, 91/271/EEC), the Catalan government developed and implemented strategic plans for the treatment of all urban and industrial waste waters, in 1995 and 2002 for urban waste waters, and in 1994 for industrial waste waters (ACA, 2002a, 2003). Nowadays, waste waters from all towns with more than 2,000 inhabitants are treated, and point sources of nutrients have decreased substantially since the first plans for urban and industrial waste water were initiated (ACA, 2002a, 2003, 2005; Prat et al., 2005; Jubany, 2008). In contrast, agricultural diffuse N emissions remain largely unaddressed. For example, at Forgars monitoring station, 14 km upstream of the river mouth, the mean concentration of soluble reactive P has decreased from 0.22 mg l^{-1} in 1990–1995 to 0.07 mg l^{-1} in 2000–2004, whereas the mean concentration of nitrate has decreased only from 1.81 to 1.32 mg l^{-1} between the same two periods.

3 Methodology

3.1 The MONERIS model

MONERIS was originally developed to estimate point and diffuse annual nutrient emissions in German river catchments larger than 50 km^2 (Behrendt et al. 2000). It has

HESSD
8, 7555–7594, 2011

subsequently been applied throughout Europe, e.g., to the Elbe, Rhine (De Wit and Behrendt, 1999; De Wit, 2000), Odra (Behrendt et al., 2003; Behrendt and Dannowski, 2005), Danube (Schreiber et al., 2005), Po (Palmeri et al., 2005), Axios, Daugava, and Vistula rivers (Kronvang et al., 2007). For La Tordera, limited data availability advised against the use of a complex, dynamic model with higher temporal resolution. Resorting to a simpler conceptually-based empirical model still allowed us to assess the major emission pathways, evaluate temporal and spatial changes in nutrient emissions, and ascertain the main factors that affected nutrient mobilisation and transport to surface waters during the study period. While temporal resolution was inevitably limited, MONERIS can discern spatial patterns through the subdivision of the catchment into subcatchments.

Based on precipitation and river flow data, geographical data on catchment land uses and physical characteristics, and statistical data on nutrient inputs, MONERIS estimates annual emissions of N and P from point sources, i.e., direct industrial discharges and municipal waste water treatment plants, and through a series of diffuse pathways that comprise atmospheric deposition, erosion, surface runoff, groundwater, tile drainage and runoff from paved urban areas. Nutrient loads are estimated as nutrient emissions from the catchment minus in-stream nutrient retention. Results are expressed as tonnes of P or N per year for total load, retention, total emissions, and emissions through each of the pathways. Further details on MONERIS can be found in Behrendt et al. (2007).

MONERIS is a spreadsheet model that consists of empirical equations sought to be of general application throughout Europe (http://moneris.igb-berlin.de/). In order to facilitate model calibration, verification and sensitivity analysis, we developed a version of the model, Rmoneris, that was completely rewritten in the R statistical programming language (http://www.r-project.org/). Besides the model itself, Rmoneris includes utilities for calibration, verification, plotting, mapping, and statistical analysis of input and output data. Rmoneris reads and outputs data in comma delimited text files that can be easily read and edited with standard spreadsheet software. Rmoneris differs from

HESSD
8, 7555–7594, 2011

MONERIS only slightly in how in-stream nutrient retention is estimated, as discussed in the calibration section below. All other equations are as described in Behrendt et al. (2007). In the remainder of the paper, when we refer to the model MONERIS the calculations discussed have been made with Rmoneris.

3.2 Model setup

In MONERIS, nutrient emissions and in-stream retention are estimated for each subcatchment, and are then accumulated down the stream network. In the present study, La Tordera was divided into 28 subcatchments following a study of ecological flows carried out by the Catalan Water Agency using the Sacramento model (ACA, 2004, 2005; Mas-Pla, 2006). The subdivision was based on the location of gauging stations and homogeneity in the hydrological response of the subcatchments. This division was adopted in our application of MONERIS in order to take advantage of modelled discharge for all 28 subcatchments (Fig. 3).

Nutrient emissions and loads were estimated yearly from 1996 to 2002. The selection of this modelling period was based on data availability. Modelled discharge data was not available after 2002, while monitoring data were highly variable before 1996, probably reflecting episodic point discharges of untreated urban and industrial sewage.

MONERIS requires a variety of input data for each subcatchment. These are discussed below. Whenever available, data were compiled yearly.

Spatial input data

The model needed not only an inventory of the limits of the catchment, subcatchments and administrative areas, i.e., municipalities and counties, and the river network, but also an inventory of the monitoring and gauging stations, waste water treatment plants (WWTPs) and major industries. These data were made available by the Catalan Cartographic Institute (ICC, http://www.icc.es/) and the Catalan Water Agency

HESSD
8, 7555–7594, 2011

(ACA, http://mediambient.gencat.net/) (Fig. 3). Total stream length in each basin was estimated from these digital maps.

Land use data were obtained from the ICC, which compiles five-yearly land use maps of Catalonia (1992, 1997 and 2002, for the study period) based on Landsat imagery (30 m cell size). Figure 1 shows the distribution of major land uses in the catchment in 1997. From these maps, we obtained the area (km^2) of each land use for the 28 subcatchments and for the three different periods. For modelling purposes, irrigated agricultural areas for the 28 subcatchments were assumed to be tile drained lands.

To estimate nutrient inputs into surface waters by erosion, the model required the mean slope, which was mapped for the 28 subcatchments from a 30 m cell size digital elevation model (DEM) obtained from ICC. Data on in-situ soil loss ($t\,yr^{-1}$) were obtained from the PESERA (Pan-European Soil Erosion Risk Assessment) map of soil erosion by water (Kirkby et al., 2004; http://eusoils.jrc.ec.europa.eu). This map is based on the European Soil Database, CORINE land cover, climate data from the MARS project and a DEM (Kirkby et al., 2004).

The hydrogeology of the subcatchments is represented in MONERIS as four classes resulting from a combination of good or poor porosity and shallow or deep groundwater; these were obtained by digitising the hydrogeological map of Catalonia for the Tordera catchment (SGC, 1992).

Because of a lack of good resolution maps of soil texture (percent sand, clay, loam, and silt) for the study area, our estimates were based on various studies conducted on an area adjacent to and partially including La Tordera catchment (Danés, 1984; Castro-Doria, 1996) and on the European Soil Database (http://eusoils.jrc.ec.europa.eu). Data on the nitrogen and phosphorus content in topsoil (%) was not available for the study area either; therefore, an estimate was produced based on the best judgment of experts from the Catalan Department of Agriculture (DARP) and the Institute for Food and Agricultural Research and Technology (IRTA).

HESSD
8, 7555–7594, 2011

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◀| |▶
◀ ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

Point source data

All data required by the model to estimate nutrient emissions from the urban and industrial waste water treatment plants (WWTP), such as year of implementation or changes in operation, outflow discharge, annual loads of N and P, and nutrient removal efficiency, were provided by the ACA. Whenever data on discharge and nutrient concentration in a WWTP outflow was deemed insufficient, of low quality or simply unavailable, WWTP loads were estimated from data on inhabitant equivalents, mean domestic and industrial N and P per capita emissions, and WWTP efficiency.

The collection of statistics on industrial waste waters not connected to municipal WWTPs by the ACA started officially in 2001 and was first published in 2003 as part of the new strategic plan for the treatment of all industrial waste waters, i.e., PSARI 2003 (ACA, 2003). No data were available before 2001.

Monitoring data

Model performance was calibrated against observed nutrient loads. These were estimated from monthly measurements conducted by ACA at selected monitoring stations (Fig. 3). These data included the following nutrient concentrations: nitrate (NO_3^-), nitrite (NO_2^-), ammonia (NH_4^+), Kjeldahl nitrogen (TKN), soluble reactive phosphorus (SRP), and total phosphorus (TP). Data for TP was unavailable or scattered before 2002, and TKN measurements were too scarce to be used for load estimation. Therefore, the model was calibrated against dissolved inorganic nitrogen (DIN, the molar sum of nitrogen as nitrate, nitrite and ammonia), and SRP. Out of the 22 monitoring stations in La Tordera, some were out of service, others provided data only from the end of the 1990s, and for all of them, data collection was somewhat irregular, especially during the 1990s. Eight stations had sufficient data for calibration (see “Calibration process” below).

Data on discharge and precipitation per subcatchment were needed to run the model. Discharge is used in the model to estimate groundwater and lateral discharge from the subcatchment water balance, and for the estimation of observed loads. Precipitation is used in the estimation of surface runoff, erosion and urban diffuse sources. Mean annual discharge (Q, $m^3 s^{-1}$) for each subcatchment were obtained from ACA's analysis of ecological flows for the internal catchments of Catalonia, where the Sacramento hydrological model was calibrated in each catchment against monthly discharge from existing gauging stations, and then used to estimate discharge for each of the 28 subcatchments defined for La Tordera (ACA, 2002b).

Data on mean annual precipitation (mm) for each subcatchment were also obtained from ACA (2002b), which provided mean precipitation spatially interpolated for each subcatchment from the 6 meteorological stations within or around the catchment (Fig. 2).

Statistical data at the administrative level

Statistical data at the municipality and regional levels that were required by the model, including data on population, crops, and livestock, were provided by the city halls and the Catalan Statistical Institute (IDESCAT).

The number of inhabitants in urban areas connected to sewage systems was estimated from information provided by the strategic plan for the treatment of all urban waste waters, i.e., PSARU (ACA, 2002a), and the concerned city halls. The following classification was used: connected to combined sewers; connected to sewers but not to WWTPs; and connected to neither WWTP nor sewer. These data were only available for the year 2001 (PSARU 2002) (ACA, 2002a). Therefore, we used 2001 as a baseline against which we corrected for changes in connected inhabitants in previous years based on the year of implementation of WWTPs and the number of inhabitants per subcatchment.

Nitrogen surplus, i.e., the balance between nitrogen inputs, mainly through atmospheric deposition, N fixation and fertiliser application, and outputs, mainly through harvest and ammonia volatilisation, is a key predictor of the nitrogen load that is potentially mobilised and transported to surface waters. It is also notoriously difficult to estimate with any accuracy. We used the OECD/Eurostat Soil Surface balance method (OECD, 2001). This method combines the use of statistics on crop harvests and the number of farm animals together with agronomic technical coefficients and land cover data to estimate nitrogen inputs to and outputs from each subcatchment. The DARP, the National Association of Fertiliser Producers (ANFFE) and waste managers were the main sources of data on fertilisers, manure farming production, and also on P and N content in topsoil. Statistics on livestock were provided by the IDESCAT. Data on sewage sludge were provided by the ACA.

Oxidised and reduced nitrogen atmospheric deposition rates (NO_x, NH_x, $\mathrm{kg\,N\,ha^{-1}\,yr^{-1}}$) were obtained from the Cooperative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe (EMEP, http://www.emep.int/). From point measurements, the Unified EMEP model generates a $50 \times 50\,\mathrm{km}^2$ resolution grid that is available at yearly resolution for the study period.

3.3 Calibration and verification process

Among the twenty-two monitoring stations in the basin, we selected the eight stations that had both regular collection of SRP and DIN concentration data and daily discharge time series from 1996 to 2002 (Fig. 3). Nutrient loads were estimated as the product of flow-weighted mean concentration and mean annual discharge:

$$L = \frac{\sum_{i=1}^{n} C_i Q_i}{\sum_{i=1}^{n} Q_i} \cdot \bar{Q}_\mathrm{N} \tag{1}$$

HESSD
8, 7555–7594, 2011

where L is the annual load of phosphorus or nitrogen ($\mathrm{t\,yr^{-1}}$), C_i is the concentration of SRP or DIN ($\mathrm{mg\,l^{-1}}$), Q_i is the daily flow, n is the number of days with concentration data, and $\overline{Q}_N$ is the mean daily flow in the hydrological year (defined from 1 October through 30 September).

MONERIS is a calibrated model and, although one would ideally want to recalibrate all its empirical parameters, this is not possible when data are scant. In this application, the number of observed data points was 56 at best (8 stations times 7 yr), so calibrating more than two or three parameters would have quickly compromised statistical power. Therefore, the strategy followed here was to calibrate the minimum number of parameters that would yield an acceptable fit (i.e., $E > 0.8$, see below).

MONERIS estimates loads as the difference between catchment emissions and in-stream retention processes. Retention accounts for the fact that modelled emissions from the catchment generally overestimate observed nutrient loads due to temporary storage or permanent losses of nutrients occurring in the river network and riparian areas (Behrendt et al., 2002, Alexander et al., 2000; Howarth et al., 2002). Retention can be very high, especially in headwater catchments, where low flows allow contact between the nutrients in transport and the biologically active streambed (Peterson et al., 2001; Martí et al., 2006; Hejzlar et al., 2009). Because retention processes are important in small catchments such as La Tordera (von Schiller et al., 2008), in this application we calibrated MONERIS for nutrient retention parameters. Specifically, nutrient retention was modelled as a function of specific runoff (discharge divided by catchment area, $\mathrm{l\,s^{-1}\,km^{-2}}$) (Behrendt and Opitz, 2000), and the parameters α and β were calibrated independently for P and N according to the following equation:

$$R = 1 - \frac{1}{1 + \beta \cdot (Q/A)^{\alpha}} \tag{2}$$

where R is the fraction of emissions that is retained in the stream network, Q is discharge ($\mathrm{l\,s^{-1}}$), and A is catchment area in $\mathrm{km^2}$.

HESSD
8, 7555–7594, 2011

Modelling nitrogen and phosphorus loads

F. Caille et al.

Calibration was performed by direct search in a limited parameter space after visual exploration of potential parameter values. The objective function for calibration was the Nash-Sutcliffe coefficient of efficiency, E (Nash and Sutcliffe, 1970):

$$E = 1 - \frac{\sum_{i=1}^{n} (O_i - P_i)^2}{\sum_{i=1}^{n} (O_i - O_{\text{avg}})^2} \quad (3)$$

where O_i is the observed data point, P_i is the modelled data point, O_{avg} is the mean of the observed data series, and n is the number of data points. E is preferred over correlation or linear regression's R^2 as a measure of goodness-of-fit because it penalises deviations from the 1:1 relationship between observed and modelled values (i.e., systematic biases in modelled values). In the calibration process, E was evaluated on log-transformed observed and modelled loads. The log transformation was required by the biased distribution of loads and the multiplicative nature of errors in catchment models (Grizzetti et al., 2005). After automatic calibration, the obtained parameter set was tweaked manually to improve the fit on loads vs. time graphs.

To verify the robustness of the model fit, automatic calibrations were run on all combinations of four years out of the seven years in the 1996–2002 period, i.e., 35 model combinations, and the model was run after each calibration on the three remaining years in the series.

3.4 Uncertainty and sensitivity analysis

Evaluating uncertainty is crucial to assessing the reliability of the estimates produced by a model (Rode and Suhr, 2007). Our analysis was based on a qualitative assessment of the reliability of input data. Input data were assigned a score based on its perceived quality. Thus, each source of data was assigned a reliability rating from 1 to 5, where 1 means most reliable and 5 means least reliable.

HESSD
8, 7555–7594, 2011

Sensitivity analysis complements uncertainty analysis by providing information on the influence of model inputs or parameters on model outputs (Saltelli et al., 2000; Brown et al., 2001). By showing how the model behaviour responds to changes in parameter values, i.e., by providing information on the factors that most strongly contribute to the output variability, sensitivity analysis not only allows the relative influence of inputs to be assessed, but also provides a good basis for future scenario testing (Brown et al., 2001).

In this application we focused on the sensitivity of the model to variations in input data. For each input data item that was analysed, the original data were varied from −15 % to +15 % their current values (the change applied to all subcatchments), in steps of 5 %, and the calibrated model was subsequently run. The set of input data included in the sensitivity analysis was: P deposition, NO_x deposition, NH_x deposition, annual precipitation, winter precipitation, summer precipitation, evaporation rate, on site soil loss, mean slope, sediment area ratio, P and N content in topsoil, tile drained area, N surplus, and number of inhabitants.

4 Results

4.1 Model calibration and verification

The calibration was performed for the hydrological years 1996 to 2002. The original version of MONERIS used two different retention coefficients, one for diffuse sources in the stream network, and one for point sources and inputs from upstream catchments, which applied only to the main channel. After several calibration attempts, in this application a single retention factor was applied to all emissions. Main channel retention of inputs from upstream catchments was found to be almost negligible, and adjusted to a factor of 2 % retention.

Also, inspection of observed and modelled data versus year revealed a significant underestimation of loads for the early years when the model was calibrated against

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper |

HESSD

8, 7555–7594, 2011

Modelling nitrogen and phosphorus loads

F. Caille et al.

later years. We attributed this to the fact that direct industrial inputs were available only for 2001 but could be expected to be greater as one moved back in time. To correct for this bias, which reflected an uncertainty in input data, the model was calibrated for a correction factor that increased industrial inputs yearly from 2001 backwards towards 1996. This substantially improved the model fit.

After calibration, the modelled annual P and N loads showed good agreement with the observed loads (Fig. 4), as measured by the Nash-Sutcliffe coefficients ($E = 0.85$ for P, and $E = 0.86$ for N). Furthermore, the deviation between modelled and observed values was lower than 30 % on a log scale. The calibrated retention parameters were similar for both N and P and within the ranges reported by Behrendt et al. (2007) (P: $\alpha = -1$, $\beta = 3.2$; and N: $\alpha = -1.3$, $\beta = 6$), resulting in mean retention factors of 46 % for P (90 % of values between 25 % and 62 %) and 52 % for N (90 % of values between 24 % and 72 %).

Inspection of model fit to interannual variation and trends in the eight calibration subcatchments showed good overall agreement between model and observed loads, but also systematic biases for some subcatchments (Fig. 5). P and N loads were better modelled in the four stations closest to the river mouth along the main channel (Fig. 3). The greatest disagreement between modelled and observed loads corresponded to the evolution of P and N loads at subcatchment 14024, where the model almost consistently overestimated observed values. Also modelled N loads at subcatchment 14023 did not fit the observed trend between 1996 and 2000 (Fig. 5). The general trend from 1996 to 2002 was a reduction of P and N loads with some fluctuations for the eight sub-basins.

The verification of the model showed that the calibration was not unduly sensitive to the selection of a calibration period, which was a concern because interannual catchment hydrology variability is large in Mediterranean climates. Mean Nash-Sutcliffe efficiencies for verification sets were slightly lower than efficiencies for calibration sets for P, and were more variable for N than for P. In all cases, however, E values were above 0.75 (Fig. 6).

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper |

HESSD

8, 7555–7594, 2011

Modelling nitrogen and phosphorus loads

F. Caille et al.

Title Page
Abstract Introduction
Conclusions References
Tables Figures
◀| |▶
◀ ▶
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

4.2 Partitioning of nutrient emissions

P emissions were dominated by urban and industrial sources, which together accounted for about 94 % of total emissions in 1996–2002 (Table 1). Among the other sources of emissions, groundwater flow contributed about 2–3 % of total P emissions, varying between 1.4 and 3.68 $t\,yr^{-1}$ during the study period. Erosion, surface runoff, tile drainage and atmospheric deposition contributed together only around 3.5 % of P emissions. The partitioning of the P emissions among subcatchments correlated with the land use distribution, with high P emissions along the main valley and lower Tordera (Table 1 and Fig. 1).

According to the model, total P emissions into La Tordera river basin decreased by about 42 % during the 1996–2002 study period (Table 1), corresponding to a decrease of about 10 % per year between 1998 and 2001 and about 7 and 4 % for 1997 and 2002 respectively. The decrease of P emissions during the study period was mainly the result of reductions in industrial and urban sources. Nonetheless, these sources remained the most important pathways of P emissions, with a contribution of 92 % of the total P emissions in the catchment in 2002. Loads from WWTPs declined over the period despite an increase in connected inhabitants.

In contrast to P emissions, N emissions were dominated by inputs via groundwater (31 % of N emissions on average during the study period), followed by urban and industrial sources, which together contributed around 58 % of total emissions in 1996–2002 (Table 1). Tile drainage was another source of consideration, with a contribution around 8.6 %. The remaining sources of emissions (erosion, surface runoff, tile drainage and atmospheric deposition) contributed together only 2 % of N emissions. The partitioning of the N emissions among subcatchments correlated with land use distribution (Table 1 and Fig. 1), with substantial urban sources along the main channel and lower Tordera and significant agricultural sources especially in the Santa Coloma basin (the northeastern part of the catchment) and lower Tordera. In headwater subcatchments, groundwater sources were important in relative terms, but low in magnitude.

HESSD
8, 7555–7594, 2011

Total N emissions into the river basin decreased by about 18 % between 1996 and 2002, and were particularly low in 2000. The observed decrease in N emissions was mainly attributable to reductions in industrial and urban sources. N inputs from these two sources declined by about 56 % and 22 %, respectively, between 1996 and 2002. In most years, an increase of N emissions from WWTPs corresponded to a decrease of emissions from urban areas (i.e., from inhabitants not connected to WWTPs and diffuse urban emissions).

4.3 Model uncertainty and sensitivity to input data

Data sources related to inputs, stocks or annual surpluses of nutrients in agricultural areas received the worst reliability score in the assessment of input data uncertainty (Table 2). For instance, it was difficult to obtain data on N and P content in arable topsoil or maps of the different soil classes that are needed to derive the average nutrient concentrations in tile drained water. This was mainly due to a lack of studies in the investigated basin. Also, limited data availability on N inputs and outputs made N surplus estimates notoriously uncertain. Data on point sources improved over the course of the study period, but were overall less reliable that one might have expected, especially for industrial sources.

Results of the sensitivity analysis of model estimates of P and N loads obtained by varying selected data items by −15 % to +15 % of their actual values were mostly linear. Therefore, we chose to plot model sensitivity to 5 % increases in the input data items considered. For both P and N, annual precipitation was the input data item to which the model was most sensitive, followed by the number of inhabitants (Fig. 7). With a 5 % increase in the annual precipitation on all subcatchments, the outputs increased between 1.9 % and 6.9 % for P, and between 2.4 % and 5.6 % for N. Among the remaining data items, a 5 % increase in population caused a 0.02 % to 3.3 % increase in the modelled P load, and a 0.02 % to 2.3 % increase in the modelled N load, depending on the subcatchment. For the other parameters related to P, the changes in outputs were lower than 1 %. With regards to nitrogen, N surplus caused a

HESSD

8, 7555–7594, 2011

Modelling nitrogen and phosphorus loads

F. Caille et al.

change from 0.04 % to 1.8 % in the output with 5 % change in the input value. For tile drainage and atmospheric deposition, the changes in outputs were around 1 %, and for the other parameters, the changes in outputs were lower than 0.1 %.

5 Discussion

5.1 Patterns of nutrient loads and emissions in time and space

Over the period 1996–2002, nutrient loads, as estimated from the model and from stream monitoring data, and nutrient emissions, as estimated from the model, showed a declining trend. These reductions in nutrient emissions over time and across subcatchments were mainly the result of the implementation and improvement of urban and industrial waste water planning strategies (PSARU in 1995 and 2002 for urban waste waters, and PSARI in 1994 for industrial waste waters) (ACA, 2002a, 2003). Despite this, at the end of the study period, La Tordera was still dominated by urban and industrial effluents, whether treated or untreated, especially for P, with large emissions concentrated along the main valley and lower Tordera.

Agricultural sources follow urban and industrial emissions as the major source of P and, especially, N, but along different pathways, as it corresponds to the different chemical nature of the emissions. P has low solubility but readily adsorbs to particles, while nitrate, the main form of inorganic nitrogen in oxic waters, is highly soluble and enters subsurface and groundwater compartments with the water that infiltrates in the soils (Novotny, 2003). Accordingly, the main pathways for P from agriculture were surface runoff and erosion, while subsurface and groundwater pathways were important for N. Agricultural sources of N were high both in absolute and in relative terms in some subcatchments, especially on the low-relief, northwestern part of the catchment. The model indicates a slight decline in diffuse emissions from 1996 to 2002, probably associated with reductions in fertiliser application, as a result of the implementation of the Nitrates Directive and guidelines on best practices with regards to nitrogen fertilisers

HESSD
8, 7555–7594, 2011

(Boixadera et al., 2000). Indeed, based on the best data available for Catalonia provided by the national association of fertiliser producers (ANFFE, Asociación Nacional Fabricantes de Fertilizantes), nitrogen inorganic fertiliser application rates decreased from 73.7 kg N ha^{-1} in 1992 to 63.1 kg N ha^{-1} in 1997 and 49.2 kg N ha^{-1} in 2002. As for phosphorus, the use of fertilisers decreased from 36.5 kg P_2O_5 ha^{-1} in 1992 to 30.75 kg P_2O_5 ha^{-1} in 1997 and 26.6 kg P_2O_5 ha^{-1} in 2002. In addition, the downward trend in diffuse nitrogen emissions may also be associated to loss of agricultural land (a decrease of 19.2 % over the period 1992–2002, from 152 km^2 in 1992 to 123 km^2 in 2002) and declines in atmospheric deposition (11.8 % over the period 1990–2002). Despite all this, the impact of agricultural diffuse sources on nutrient loads remains a problem.

Interannual variability around the declining trend from 1996 to 2002 was mainly associated with variability in precipitation, the input data item to which the model was most sensitive. This is to be expected since wet years increase the effective contributing area, enhance nutrient mobilisation and transport, wash out nutrients accumulated on impervious surface areas, and raise the probability of overflows in urban areas with combined sewers (Novotny, 2003; Grizzetti et al., 2005). In the calibrated model, variability in precipitation affected most strongly in-stream nutrient retention through changes in discharge, and therefore in specific runoff.

The retention term turned out to be crucial for model calibration not only because of its sensitivity to interannual climate variability, but also because of its magnitude. According to model results, on average about 50 % of nutrient emissions are temporarily stored or permanently removed from the stream network on an annual basis. The importance of in-stream nutrient retention has been recognised both at reach (Peterson et al., 2001; Martí et al., 2004) and river network scales (Alexander et al., 2000; Behrendt and Opitz, 2000; Seitzinger et al., 2002), with retention efficiencies that are commensurate with those found in this study, especially for small basins, where low flows increase contact between nutrients in transport and the biologically active streambed (Peterson et al., 2001). Yet the high retention estimated for La Tordera is probably related to other factors. Firstly, MONERIS estimates total P and total N, whereas calibration for La Tordera was performed against dissolved inorganic P and N. Therefore, calibrated retention coefficients must include also a correction for total to dissolved inorganic forms. Secondly, MONERIS does not take into account riparian areas, which may act as hot spots for nutrient retention (Lowrance et al., 1984; Osborne and Kovacic, 1993; Krause et al., 2008), nor other forms of retention during nutrient transport across the landscape (Haag and Kaupenjohann, 2001); thus, the calibrated coefficients must also account for these forms of retention. Finally, La Tordera is a Mediterranean stream with low flow in the summer, which may even dry up on some sections in some years, and with a large fluvial aquifer in the middle and lower sections. As a losing stream, a fraction of transported nutrients must flow into the hyporheos, where they might be lost through denitrification, through lateral flow to the riparian vegetation and wetlands, or vertically as river aquifer recharge (Hancock, 2002). This could partially explain why, contrary to expectations (Peterson et al., 2001), calibrated retention efficiencies were higher in the lower Tordera than in headwaters (Fig. 8).

5.2 Uncertainties in the model application

Although the calibration and verification of MONERIS was successful, as measured by Nash-Sutcliffe efficiencies, several sources of uncertainty, that either added noise to modelled values or produced biases in load estimates, had to be recognized, identified, and, to the extent that this was possible, quantified. Uncertainties had their origin in the model structure, in observed loads and in input data.

As a calibrated, empirical, steady-state model, MONERIS is useful for large scale, rapid assessment and apportionment of loads, but has important limitations (Schoumans and Silgram, 2003). The most significant of these concerns catchment hydrology. MONERIS does not model discharge, and groundwater flow is estimated from the water balance. This is a concern especially for losing streams, as infiltration to fluvial aquifers is not considered in the water balance of the stream, and this may result in underestimated groundwater flows. In this application to La Tordera, this means

HESSD
8, 7555–7594, 2011

that diffuse nutrient sources (especially nitrogen) through groundwater flow must be viewed as conservative estimates. On the positive side, MONERIS allowed us to focus on data collection and evaluation of data quality, and provided a robust (as measured by verification) model of the major interannual and spatial patterns in nutrient emissions. In data-starved basins such as La Tordera, more complex models might not have yielded increased predictive power (De Wit and Pebesma, 2001). On the other hand, simpler statistical models (e.g., Smith et al., 1997; Grizzetti et al., 2005) could not have provided as rich an image of the catchment as MONERIS, as they would have been limited to a few parameters without regard to actual processes, posing a serious limitation on scenario development, which is the ultimate goal for the application of our model. As a conceptually-based, empirical model, MONERIS nicely bridges purely statistical models and complex process-based models.

So-called observed loads, which were used in the calibration, were of course not observed but estimated from daily discharge and nutrient concentrations. Because sampling frequency was low, i.e., monthly at best, load estimates were expected to show large errors (Littlewood, 1995; Johnes, 2007). Large variability in "observed" loads that appears trendless and was not matched by modelled loads, especially for P in headwater subcatchments, may be attributed to errors in load estimates from monitoring data rather than to errors in modelled data. In addition, according to ACA (2002b), discharge was systematically underestimated in some gauging stations, notably Fogars de Tordera (at subcatchment 14024), and this could explain why the model consistently overestimated nutrient loads at that station.

Some of the data sources for the model were remarkably unreliable, notably N and P concentrations in topsoil and N surplus. This issue highlights the deficiencies in data collection by the concerned statistical agencies. For example, despite the importance of diffuse sources for surface water quality, there does not seem to be a concerted effort to collect, with the appropriate quality controls, data on inorganic and organic fertiliser application rates. This may be partly blamed on a lack of cooperation between two governmental agencies with distinct constituencies and somewhat conflicting goals

HESSD
8, 7555–7594, 2011
Modelling nitrogen and phosphorus loads
F. Caille et al.

(i.e., the Department of Agriculture, DARP, and the ACA), as suggested by a social analysis done as part of an Integrated Environmental Assessment (Caille, 2009). In contrast, point sources are largely under the jurisdiction of the ACA; in spite of this, data on WWTP effluents and, especially, industrial effluents, was found to be wanting. Industrial point source data were only available from 2001 onwards. To correctly model temporal trends in nutrient loads, we had to assume that industrial P and N emissions were larger in the preceding years.

5.3 Uncertainty, sensitivity, and scenario development

The analysis of model uncertainty and sensitivity is useful for assessing the model's potential for exploring scenarios of the evolution of the catchment under different pressures or different management regimes. With this goal in mind, we focused on model sensitivity to input data. MONERIS was found to be most sensitive to changes in precipitation. This is to be expected, as the precipitation regime affects all diffuse emission pathways. However, MONERIS would not be suitable to explore climate change scenarios because it does not explicitly model the catchment hydrology. Among the other input data examined, the model was especially sensitive to the number of inhabitants (related to urban emission sources), on-site soil loss and P content in topsoil (related to P emissions through erosion), N surplus and tile drained area (related to N emissions from agricultural areas), and atmospheric deposition (Fig. 7). Therefore, N and P emissions should change noticeably under catchment scenarios that involve changes in any of those input data. It is worth noting that model sensitivity varies not only among nutrients, but also across subcatchments depending on their major emissions pathways, which highlights the fact that model sensitivity is always relative to a particular realisation of a model.

Analysing sensitivity to input data together with uncertainty of input data also helps identify problem areas in model application. The worst situation occurs when a model is highly sensitive to input data that are only known with uncertainty, because when this occurs, errors in source data magnify and propagate to model outputs. In the

HESSD
8, 7555–7594, 2011

application of MONERIS to La Tordera, this is the case especially for P emissions through erosion, and for N emissions originating in agricultural N surplus. Thus, model results, including scenarios, involving these pathways must be viewed with caution.

6 Conclusions

In this study, the application of the model MONERIS to the western Mediterranean catchment of La Tordera to estimate nutrient loads was successfully calibrated and validated (Nash-Sutcliffe efficiencies $E = 0.85$ for P, and $E = 0.86$ for N). The modelling of nutrient emissions to the river basin showed that P emissions were dominated by point sources, while inputs via groundwater had the greater contribution of total N emissions followed by point sources. In spite of all the potential hurdles related to the model structure, observed loads, and input data that were encountered during the modelling process, MONERIS provided a robust model of the major temporal and spatial patterns in nutrient emissions. Interannual variability observed around the declining trend was mainly associated with variability in precipitation, which affected in-stream retention, estimated to be about 50 % of nutrient emissions on an annual basis and related to many factors during nutrient transport. The understanding of these factors driving nutrient retention still requires more studies, such as analysis of riparian areas, wetlands or hyporheos.

Despite the decrease in nutrient emissions observed over time and across subcatchments for the period 1996–2002, mostly related to the implementation and improvement of urban and industrial waste water planning strategies (PSARU and PSARI), La Tordera basin is still dominated by urban and industrial effluents, especially for phosphorus. Regarding the contribution of agricultural diffuse sources to nutrient emissions, especially for nitrogen, their impact still remains a problem.

The analysis of the model uncertainty and sensitivity to input data provided a good basis to explore the evolution of the catchment under different pressures or management strategies and helped to identify problem areas in model application.

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper |

HESSD

8, 7555–7594, 2011

Acknowledgements. The authors would like to thank E. Martí and F. Sabater for their contribution in this paper, and for sharing their knowledge and experiences on nutrient flow related issues in La Tordera river basin. Funding for this project was provided by the Institute of Environmental Sciences and Technology (ICTA, UAB) and the European projects Eurolimpacs (FP6-SUSTDEV, project reference 505540) and REFRESH (FP7, project number 244121). Frédérique Caille benefited from an IQUC and Marie Curie scholarship, respectively from the Catalan government and the European Community for the Sense research school programme.

References

ACA (Agència Catalana de l'Aigua): Pla de sanejament d'aigües residuals urbanes (PSARU 2002). Departament de Medi Ambient de la Generalitat de Catalunya, 2002a.

ACA (Agència Catalana de l'Aigua): Estudi d'actualització de l'avaluació de recursos hídrics de les conques internes de Catalunya. Conques Internes de Catalunya. Document de síntesi. Departament de Medi Ambient de la Generalitat de Catalunya, 2002b.

ACA (Agència Catalana de l'Aigua): Programa de sanejament d'aigües residuals industrials (PSARI 2003). Departament de Medi Ambient de la Generalitat de Catalunya, 2003.

ACA (Agència Catalana de l'Aigua): Pla sectorial de cabals de manteniment de las conques internes de Catalunya. Departament de Medi Ambient i Habitatge de la Generalitat de Catalunya, 2004.

ACA (Agència Catalana de l'Aigua): Caracterizació de masses d'aigua i anàlisi del risc d'incompliment dels objectius de la Directiva Marc de l'Aigua (2000/60/CE) a Catalunya, Documento Impress. Departament de Medi Ambient de la Generalitat de Catalunya, available on-line at: http://mediambient.gencat.net/aca/ca//planificacio/directiva/impress.jsp, 2005.

Addiscott, T. M.: Simulating modelling and soil behaviour, Geoderma, 60, 15–40, 1993.

Addiscott, T. M. and Mirza, N. A.: Modelling contaminant transport at catchment or regional scale, Agriculture, Ecosystems & Environment, 67, 211–221, 1998.

Alexander, R. B., Smith, R. A., and Schwarz, G. E.: Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico, Nature, 403, 758–761, 2000.

Arheimer, B. and Brandt, M.: Modelling nitrogen transport and retention in the catchments of Southern Sweden, Ambio, 27(6), 471–480, 1998.

Arnold, J. G., Srinivasan, R., Muttiah, R. S., and Williams, J. R.: Large area hydrologic modeling and assessment. Part I. Model development, J. Am. Water Resour. As., 34, 73–89, 1998.

HESSD

8, 7555–7594, 2011

Modelling nitrogen and phosphorus loads

F. Caille et al.

Behrendt, H. and Dannowski, R.: Nutrients and heavy metals in the Odra River system, Weißensee Verlag, Berlin, 353 pp., 2005.
Behrendt, H. and Opitz, D.: Retention of nutrients in river systems: dependence on specific runoff and hydraulic load, Hydrobiologia, 410, 111–122, 2000.
Behrendt, H., Huber, P., Kornmilch, M., Opitz, D., Schmoll, O., Scholz, G., and Uebe, R.: Nutrient emissions into river basins of Germany. UBA-Texte 23/00: 1-288, Umweltbundesamt Berlin, Berlin, 2000.
Behrendt, H., Kornmilch, M., Opitz, D., Schmoll, O., and Scholz, G.: Estimation of the nutrient inputs into river systems – experiences from German rivers, Regional Environmental Change, 3, 107–117, 2002.
Behrendt, H., Dannowski, R., Deumlich, D., Dolezal, F., Kajewski, I., Kornmilch, M., Korol, R., Mioduszewski, W., Opitz, D., Steidl, J., and Stronska, M.: Point and diffuse emissions of pollutants, their retention in the river system of the Odra and scenario calculations on possible changes, Weißensee Verlag, 300 pp., 2003.
Behrendt, H., Venohr, M., Hirt, U., Hofmann, J., Opitz, D., and Gericke, A.: The model system MONERIS, version 2.0, User's manual. Leibniz Institute of Freshwater Ecology and Inland Fisheries in the Forschungsverbund Berlin e.V., Berlin, Germany, 2007.
Billen, G. and Garnier, J.: Nitrogen transfers through the Seine drainage network: a budget based on the application of the 'Riverstrahler' model, Hydrobiologia, 410, 139–150, 2000.
Boixadera, J., Sió, J., Àlamos, M., and Torres, E.: Manual del codi de bones pràtiques agràries: nitrogen. Departament d'Agricultura, Ramaderia i Pesca, Direcció General de Producció Agrària i Innovació Rural de la Generalitat de Catalunya, Lleida – Barcelona, Novembre 2000.
Brown, L., Armstrong Brown, S., Jarvis, S. C., Syed, B., Goulding, K. W. T., Phillips, V. R., Sneath, R. W., and Pain, B. F.: An inventory of nitrous oxide emissions from agriculture in the UK using the IPCC methodology: emission estimate, uncertainty and sensitivity analysis, Atmos. Environ., 35, 1439–1449, 2001.
Caille, F.: Integrated environmental assessment of nutrient emissions in a Mediterranean catchment: A case study in La Tordera, Catalonia. PhD Thesis, Autonomous University of Barcelona, Bellaterra, Spain, available on-line at: http://cataleg.uab.cat/, 2009.
Caille, F., Riera, J. L., Rodríguez-Labajos, B., Middelkoop, H., and Rosell-Melé, A.: Participatory scenario development for integrated assessment of nutrient flows in a Catalan river catchment, Hydrol. Earth Syst. Sci., 11, 1843–1855, doi:10.5194/hess-11-1843-2007, 2007.

Castro-Doria, F. X.: Mapa de los suelos forestales de la comarca La Selva [Map of Forest Soils of La Selva County] (unpublished, bachelor's degree final project), 1996.
Conan, C., Bouraoui, F., Turpin, N., de Marsily, G., and Bidglio, G.: Modelling flow and nitrate fate at catchment scale in Britany (France), J. Environ. Qual., 32(6), 2026–2032, 2003.
Danés, R., Boixadera, J., Julià, R., Roca, J., De Bolós, O., and Montserrat, J. M.: Catàleg de sòls de la circumscripció de Barcelona: Terme municipal: Fogars de Tordera, Servei d'agricultura i Ramaderia, Published by the Diputació de Barcelona, Institut d'Edicions, Barcelona, ISBN No. 84-500-9944-7, available on-line at: http://www.diba.es/iep/iep_recerca_titol.asp, 1984.
De Wit, M.: Modelling nutrient fluxes from source to river load: a macroscopic analysis applied to the Rhine and Elbe basins, Hydrobiologia, 410, 123–130, 2000.
De Wit, M. and Behrendt, H.: Nitrogen and phosphorus emissions from soil to surface water in the Rhine and Elbe basins, Water Sci. Technol., 39(12), 109–116, 1999.
De Wit , M. J. M., and Pebesma, E. J.: Nutrient fluxes at the river basin scale. II: the balance between data availability and model complexity, Hydrol. Process., 15(5), 761–775, 2001.
EEA (European Environmental Agency): Nutrients in European ecosystems. Environmental assessment report No 4. European Environmental Agency, Copenhagen, 1999.
EEA (European Environmental Agency): Europe's water: an indicator-based assessment, EEA, Copenhagen, 2003.
Grizzetti, B., Bouraoui, F., de Marsily, G., and Bidoglio, G.: A statistical method for source apportionment of riverine nitrogen loads, J. Hydrol., 304, 302–315, 2005.
Haag, D. and Kaupenjohann, M.: Landscape fate of nitrate fluxes and emissions in Central Europe: A critical review of concepts, data, and models for transport and retention, Agriculture, Ecosystems & Environment, 86(1), 1–21, 2001.
Hancock, P. J.: Human Impacts on the Stream-Groundwater Exchange Zone, Environ. Manage., 29(6), 763–781, 2002.
Hejzlar, J., Anthony, S., Arheimer, B., Behrendt, H., Bouraoui, F., Grizzetti, B., Groenendijk, P., Jeuken, M. H. J. L., Johnsson, H., Lo Porto, A., Kronvang, B., Panagopoulos, Y., Siderius, C., Silgram, M., Venohr, M., and Zaloudík, J.: Nitrogen and phophorus retention in surface waters: an inter-comparison of predictions by catchment models of different complexity, J. Environ. Monitor., 11(3), 584–593, 2009.
Hetling, L. J., Jaworski, N. A., and Garretson, D. J.: Comparison of nutrient input loading and riverine export fluxes in large watersheds, Water Sci. Technol., 39, 189–196, 1999.

HESSD
8, 7555–7594, 2011

Modelling nitrogen and phosphorus loads

F. Caille et al.

Howarth, R. W., Sharpley, A., and Walker, D.: Sources of nutrient pollution to coastal waters in the United States: Implications for achieving coastal water quality goals, Estuaries, 25(4b), 656–676, 2002.

Johnes, P. J.: Uncertainties in annual riverine phosphorus load estimation: Impact of load estimation methodology, sampling frequency, baseflow index and catchment population density, J. Hydrol., 332(1–2), 241–258, 2007.

Jubany, J.: Seguiment de la qualitat biològica de l'aigua de la Tordera mitjançant la comunitat de macroinvertebrats, in: Els sistemes socioecològics de la conca de la Tordera, edited by: Boada, M., Mayo, S., and Maneja, R., ICHN, Barcelona, ISBN No. 978-84-7283-983-0, 2008.

Kirkby, M. J., Jones, R. J. A., Irvine, B., Gobin, A, Govers, G., Cerdan, O., Van Rompaey, A. J. J., Le Bissonnais, Y., Daroussin, J., King, D., Montanarella, L., Grimm, M., Vieillefont, V., Puigdefabregas, J., Boer, M., Kosmas, C., Yassoglou, N., Tsara, M., Mantel, S., Van Lynden, G. J., and Huting, J.: Pan-European Soil Erosion Risk Assessment: The PESERA Map, Version 1 October 2003. Explanation of Special Publication Ispra 2004 No.73 (S.P.I.04.73). European Soil Bureau Research Report No.16, EUR 21176, 18pp. and 1 map in ISO B1 format. Office for Official Publications of the European Communities, Luxembourg, 2004.

Krause, S., Jacobs, J., Voss, A., Bronstert, A., and Zehe, E.: Assessing the impact of changes in landuse and management practices on the diffuse pollution and retention of nitrate in a riparian floodplain, Science of The Total Environment, 389(1), 149–164, 2008.

Kronvang, B., Grant, R., Larsen, S. E., Svendsen, L. M., and Kristensen, P.: Non-point source nutrient losses to the aquatic environment in Denmark. Impact of agriculture, Marine and Freshwater Research, 46, 167–177, 1995.

Kronvang, B., Vagstad, N., Behrendt, H., Bøgestrand, J., and Larsen, S. E.: Phosphorus losses at the catchment scale within Europe: an overview, Soil Use and Management, 23 (Suppl. 1), 104–116, 2007.

Littlewood, I. G.: Hydrological regimes, sampling strategies, and assessment of errors in mass load estimates for United Kingdom Rivers, Environ. Int., 21(2), 211–220, 1995.

Lowrance, R., Todd, R., Fail, J. Jr., Hendrickson, O. Jr., Leonard, R., and Asmussen, L.: Riparian forests as nutrient filters in agricultural watersheds, BioScience, 34(6), 374–377, 1984.

Luzón, J. L., Vila, J., and Rubio, F.: El papel de la delimitación de las Regiones Metropolitanas en el proceso de planificación: El caso de Barcelona. In: Transformaciones regionales y urbanas en Europa y América Latina. Coordinated by Luzón, J. L., Stadel, C., and C. Borges.

HESSD
8, 7555–7594, 2011

Server de Publicacions de la Universitat de Barcelona, 2003.
Martí, E., Aumatell, J., Godé, Ll., Poch, M., and Sabater, F.: Nutrient Retention Efficiency in Streams Receiving Inputs from Wastewater Treatment Plants, J. Environ. Qual., 33, 285–293, 2004.
Martí, E., Sabater, F., Riera, J. L., Merseburger, G. C., von Schiller, D., Argerich, A., Caille, F., and Fonollà, P.: Fluvial nutrient dynamics in a humanized landscape. Insights from a hierarchical perspective, Limnetica, 25(1–2), 513–526, 2006.
Mas-Pla, J.: Aspectos hidrológicos de la Directiva Marco del Agua, in: La directiva marc de l'aigua a Catalunya. Conceptes, reptes i expectatives en la gestió dels recursos hídrics, edited by: Mas-Pla, J., Consell Assessor per al Desenvolupament Sostenible de Catalunya, Generalitat de Catalunya, ISBN No. 84-393-7127-6, 107–124, 2006.
Nash, J. E. and Sutcliffe, J. V.: River flow forecasting through conceptual models: Part I. A discussion of principles, J. Hydrol., 10, 282–290, 1970.
Novotny, V.: Water Quality. Diffuse Pollution and Watershed Management, John Wiley & Sons, New York, 2003.
OECD: OECD National Soil Surface Nitrogen Balances – Explanatory notes. OECD, 20 pp., Paris, available on-line at: http://www.oecd.org/dataoecd/0/11/1916652.pdf, March, 2001.
Osborne, L. L. and Kovacic, D. A.: Riparian vegetated buffer strips in water-quality restoration and stream management, Freshwater Biology, 29, 243–58, 1993.
Palmeri, L., Bendoricchio, G., and Artioli, Y.: Modelling nutrient emissions from river systems and loads to the coastal zone: Po River case study, Italy, Ecological Modelling, 184, 37–53, 2005.
Peterson, B. J., Wollheim, W. M., Mulholland, P. J., Webster, J. R., Meyer, J. L., Tank, J. L., Martí, E., Bowden, W. B., Valett, H. M., Hershey, A. E., Mcdowell, W. H., Dodds, W. K., Hamilton, S. K., Gregory, S., and Morrall, D. D.: Control of nitrogen export from watersheds by headwater streams, Science, 292, 86–90, 2001.
Pieterse, N. M., Bleuten, W., and Jørgensen, S. E.: Contribution of point sources and diffuse sources to nitrogen and phosphorus loads in lowland river tributaries, J. Hydrol., 271, 213–225, 2003.
Prat, N., Vila-Escalé, M., Jubany, J., Miralles, M., and Ordeix, M.: Qualitat ecològica del Llobregat, el Besòs, el Foix, la Tordera i el Ter: Informe 2003. Published by the Diputació de Barcelona, Institut d'Edicions, Barcelona, ISBN No. 84-9803-070-6, 2005.
Rode, M. and Suhr, U.: Uncertainties in selected river water quality data, Hydrol. Earth Syst.

HESSD
8, 7555–7594, 2011

Modelling nitrogen and phosphorus loads

F. Caille et al.

Sci., 11, 863–874, doi:10.5194/hess-11-863-2007, 2007.
Saltelli, A., Chan, K., and Scott, M. (Eds): Sensitivity Analysis. John Wiley and Sons publishers, Probability and Statistics series, 2000.
Schoumans, O. F. and Silgram, M.: Review and literature evaluation of quantification tools for the assessment of nutrient losses at catchment scale. EUROHARP report 1-2003, NIVA report SNO 4739-2003, Oslo, Norway, ISBN No. 82-557-4411-5, 120 pp., 2003.
Schreiber, H., Behrendt, H., Constantinescu, L. T., Cvitanic, I., Drumea, D., Jabucar, D., Juran, S., Pataki, B., Snishko, S., and Zessner, M.: Nutrient emissions from diffuse and point sources into the river Danube and its main tributaries in the period 1998–2000: results and problems, Water Sci. Technol., 51, 3–4, 283–290, 2005.
Seitzinger, S. P., Styles, R. V., Boyer, E. W., Alexander, R. B., Biller, G., Howarth, R. W., Mayer, B., and Van Breemen, N.: Nitrogen retention in rivers: model development and application to watersheds in the northeastern U.S.A., Biogeochemistry, 57/58, 199–237, 2002.
SGC: Mapa d'àrees hidrogeològiques de Catalunya 1:250 000 [Hydrogeological Map of Catalonia]. Servei Geològic de Catalunya, Institut Cartogràfic de Catalunya. 1a ed., Barcelona , ICC, 1992.
Smith, R. A., Schwarz, G. E., and Alexander, R. B.: Regional interpretation of water-quality monitoring data, Water Resour. Res., 33, 2781–2798, 1997.
Soja, E.: Postmetropolis. Critical studies of Cities and Region. Blackwell, London, 2000.
Vitousek, P. M., Aber, J., Howarth, R. W., Likens, G. E., Matson, P. A., Schindler, D. W., Schlesinger, W. H., and Tilman, G. D.: Human alteration of the global nitrogen cycle: causes and consequences, Ecological Applications, 7, 737–750, 1997.
Von Schiller, D., Martí, E., Riera, J. L., Ribot, M., Argerich, A., Fonollà, P., and Sabater, F.: Interannual, annual, and seasonal variation of P and N retention in a perennial and an intermittent stream, Ecosystems, 11(5), 670–687, 2008.
WFD CIS Guidance Document No. 3: Analysis of Pressures and Impacts. Published by the Directorate General Environment of the European Commission, Brussels, ISBN No. 92-894-5123-8, ISSN No. 1725–1087, Dec 2002.
Whitehead, P. G., Wilson, E. J., and Butterfield, D.: A semi-distributed Integrated Nitrogen model for multiple source assessment in Catchment (INCA). Part I. Model structure and process equations, Sci. Total Environ., 210/211, 547–558, 1998.
Whitmore, A. P., Bradbury, N. J., and Johnson, P. A.: Potential contribution of ploughed grassland to nitrate leaching, Agriculture, Ecosystems and Environment, 39, 221–233, 1992.

Table 1. Contribution of the different sources to the emissions of phosphorus and nitrogen into the river basin in tonnes/yr and as a percentage of the total emissions in the basin. Two periods, 1997–1999 and 2000–2002, are used to show changes in the estimation of nutrient emissions based on the year 1996, the first reliable year of model application.

Pathway	Phosphorus Emissions						Nitrogen Emissions					
	1996		1997–1999		2000–2002		1996		1997–1999		2000–2002	
	t/yr	%	t/yr	%	t/yr	%	t/yr	%	t/yr	%	t/yr	%
WWTP	14.6	12.7	14.5	14.9	10.5	14.7	91.2	12.1	108.3	16.0	117.7	19.7
Industry	64.4	56.0	52.4	53.7	34.5	48.4	171.7	22.8	139.8	20.7	91.9	15.4
Urban system	29.1	25.3	25.1	25.8	21.9	30.8	174.8	23.2	150.2	22.2	130.3	21.8
Atm. deposition	0.1	0.1	0.1	0.1	0.1	0.1	2.9	0.4	2.8	0.4	2.9	0.5
Surface runoff	1.6	1.4	1.1	1.1	0.7	1.0	14.1	1.9	9.4	1.4	7.0	1.2
Erosion	1.3	1.1	1.1	1.2	1.0	1.5	1.7	0.2	1.5	0.2	1.3	0.2
Tile drainage	0.9	0.8	0.9	0.9	0.7	1.0	62.3	8.3	57.7	8.5	51.8	8.7
GW	2.9	2.6	2.3	2.3	1.9	2.7	234.4	31.1	207.3	30.6	194.8	32.6
Total Emissions	114.9		97.6		71.3		753.3		676.9		597.7	
Retention	52.0	45.2	44.9	46.0	38.8	54.5	340.8	45.2	337.6	49.9	334.5	56.0
Estimated Load	63.0		52.7		32.5		412.5		339.4		263.2	
Observed Load	58.7		50.8		31.6		444.7		273.7		265.1	

HESSD

8, 7555–7594, 2011

Modelling nitrogen and phosphorus loads

F. Caille et al.

Table 2. Reliability rating of the sources of data. Scores range from 1 to 5, where 1 is most reliable and 5 is least reliable.

Variable	Reliability
Climatic and hydrological characteristics	
Mean annual precipitation	2
Long term annual precipitation	2
Evaporation rate	2
Mean stream discharge	2
SRP concentration	2–3
DIN concentration	2–3
Land use, except urban areas	1
Urban and industrial areas	2
Industrial and urban point sources (WWTPs)	
Mean nutrient annual loads	2–3
Mean annual effluent discharge	2
Removal efficiency of N and P	3
Connected inhabitants	2–3
Equivalent inhabitants from industries	2–3
Diffuse sources	
NO_X deposition	2
NH_4^+ deposition	2
Area of surface water	2–3
On site soil loss	2–3
P and N content of arabe topsoil	5
Mean catchment slope	1–2
Drained agricultural area	2–3
N surplus	4–5
Inorganic fertilizers	2–3

HESSD
8, 7555–7594, 2011

Modelling nitrogen and phosphorus loads

F. Caille et al.

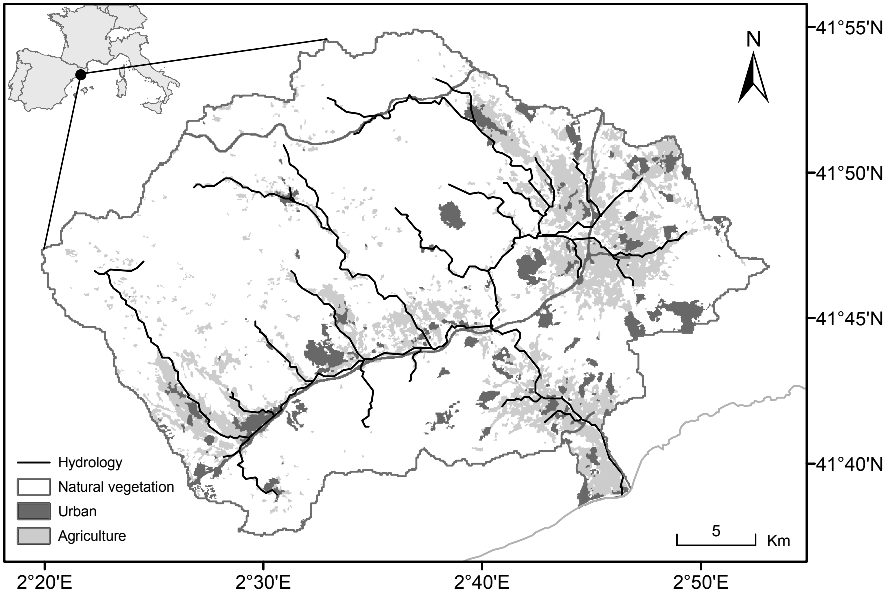

Fig. 1. Location of La Tordera catchment in Catalonia (Southern Europe) showing main land uses for the year 1997 and the river network. Source: Catalan Cartographic Institute (ICC, Institut Cartogràfic de Catalunya).

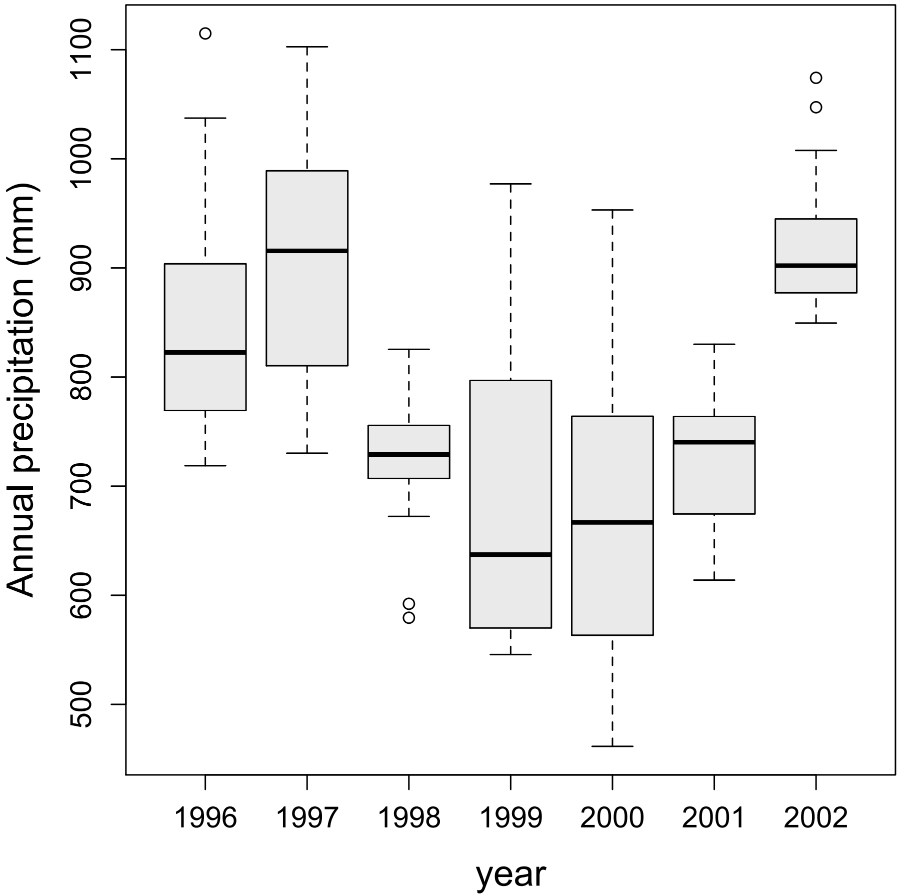

Fig. 2. Annual precipitation between 1996 and 2002 in La Tordera basin. Source: ACA.

HESSD
8, 7555–7594, 2011

Modelling nitrogen and phosphorus loads

F. Caille et al.

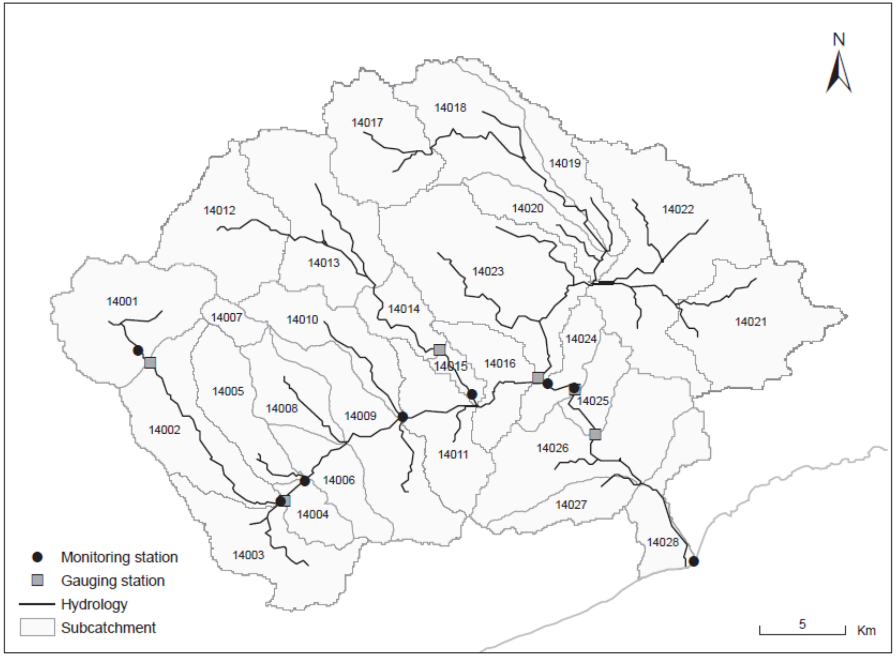

Fig. 3. Representation of the catchment and subcatchment borders with their label in La Tordera catchment, and river network with the location of the gauging stations and monitoring stations used for the calibration. Source: ICC and Catalan Water Agency (ACA, Agencia Catalana de l'Aigua).

HESSD
8, 7555–7594, 2011

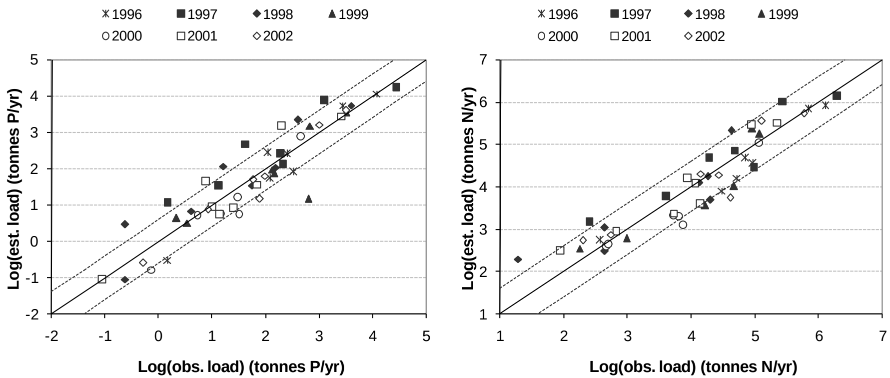

Fig. 4. Plots of modelled versus observed values of total phosphorus and total nitrogen presented in logarithmic scales for the different years of the study period. The dashed lines represent a 30 % deviation.

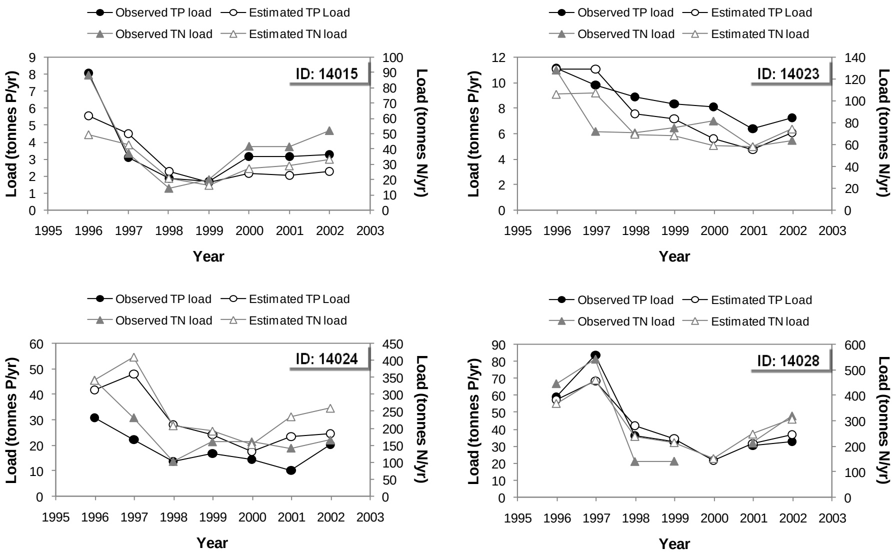

Fig. 5. Temporal evolution of observed and modelled loads of phosphorus and nitrogen for the four stations closest to the river mouth along the river, i.e., those corresponding to subcatchments 14015, 14023, 14024 and 14028 (Fig. 3).

HESSD
8, 7555–7594, 2011

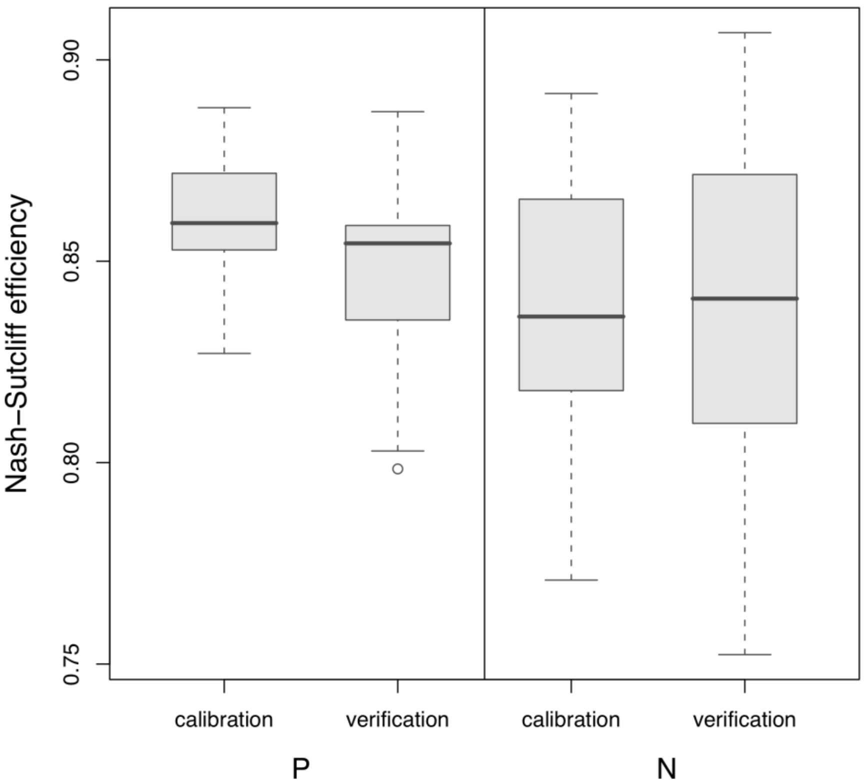

Fig. 6. Verification of Rmoneris for La Tordera. Calibration boxplots summarize Nash-Sutcliffe efficiencies for 35 automatic calibrations of the model (all combinations of four years in the period 1996–2002). Verification boxplots are for model runs with the parameter set from each calibration on the three years not used in the calibration for each of the 35 models runs.

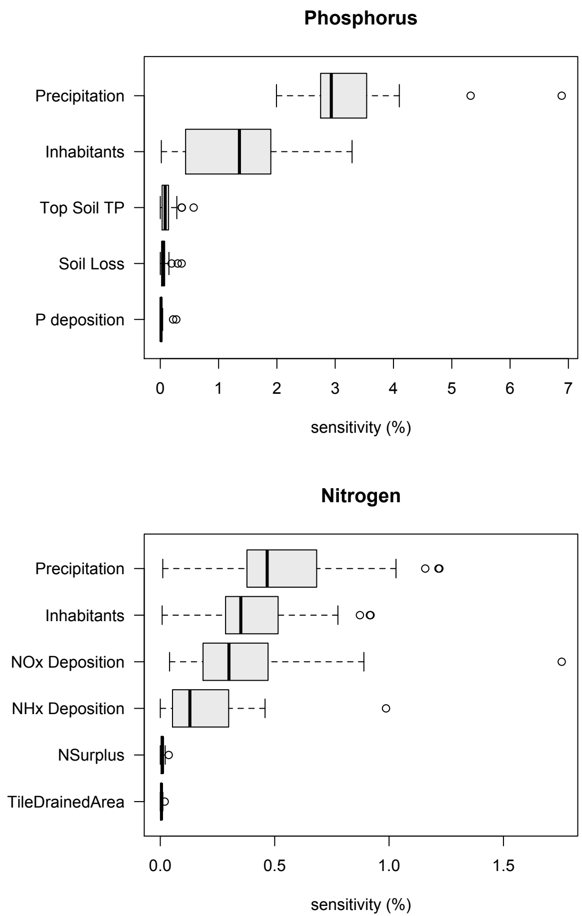

Fig. 7. Model sensitivity to input data for phosphorus and nitrogen. Input data items box plots across subcatchments summarise the sensitivity of the model.

HESSD
8, 7555–7594, 2011

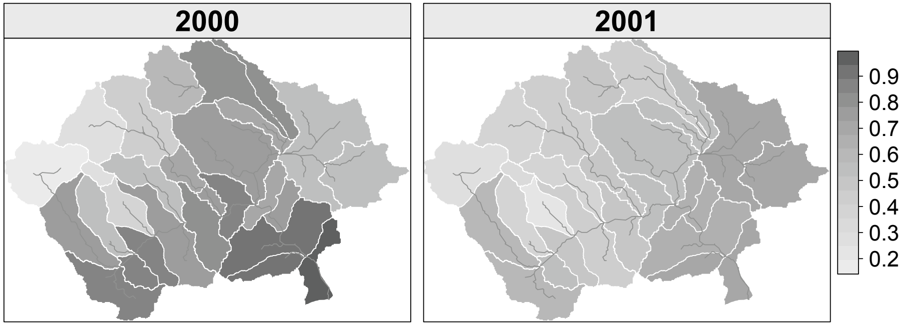

Fig. 8. Nitrogen retention (as a fraction) per subcatchment on a dry year (2000, 670 mm annual rainfall), and a wet year (2001, 727 mm annual rainfall).

HESSD
8, 7555–7594, 2011

Modelling nitrogen and phosphorus loads

F. Caille et al.