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Assessing the impact of agricultural pressures on N and P loads and eutrophication risk

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ABSTRACT

Excessive nutrient delivery into freshwater bodies results in increased eutrophication risk worldwide. Because high-frequency monitoring cannot be generalised to all rivers, methods are needed to assess eutrophication risk in contexts with scarce data. To this end, we present an assessment framework which includes: (i) a mass-balance model to estimate diffuse N and P transfer/retention in unmonitored catchments and (ii) a set of indicators based on N:P:Si molar ratios to assess the risk of eutrophication in freshwaters. The model, called Nutting, integrates variables that describe both agricultural pressures and physical attributes of catchments (climate, topography, soil). Nutting refines previous mass-balance models by describing nutrient pressures with soil N surplus and soil P content instead of N and P inputs, and by considering physical attributes not only as lumped variables over the entire area but also within river corridors. The model was calibrated on a set of 160 independent catchments across France and applied to all headwater catchments. We found that apparent N and P retention represented $53 \pm 24\%$ and $95 \pm 29\%$ of soil N and P surplus, respectively, and was mainly controlled by the climate and a hydrology-related connectivity index. The spatial organisation of the landscape was of secondary importance compared to the refined description of agricultural pressures. Estimated eutrophication risk was highly sensitive to assumptions about P bioavailability, hence the potential range of headwaters at risk of eutrophication spanned 26–63% of the catchments, depending on assumptions. This framework provides a generic method to assess the relative contribution of agriculture to nutrient loads and the subsequent risk of eutrophication.

1. Introduction

Degradation of surface water resulting from excessive nitrogen (N) and phosphorus (P) inputs is a major concern for drinking water quality and ecosystem health (Carpenter et al., 1998; Vitousek et al., 1997). Due to improvement of point-source control in recent decades, research and management efforts to decrease nutrient pollution have been redirected towards diffuse sources (Van Drecht et al., 2009). In industrialised countries, most source apportionment studies have shown that agriculture is currently a major source of nutrients in surface waters (e.g. Bouraoui and Grizzetti, 2011; Grizzetti et al., 2012; Windolf et al., 2012). Nutrient transfers from agricultural landscapes result from combined hydrological and biogeochemical processes controlling their mobilisation and delivery in the terrestrial and aquatic compartments of catchments (Bouwman et al., 2013; Haygarth et al., 2005; Seitzinger et al., 2006). These processes are difficult to understand and to model due to the complexity of agricultural landscapes (Burt and Pinay, 2005; Strayer et al., 2003).

Low-order catchments (i.e. below Strahler order 5) are known to contribute large amounts of nutrient loads to downstream water bodies (Alexander et al., 2007; Lassaletta et al., 2010; Peterson et al., 2001). In terms of scientifically understanding the processes controlling N and P diffuse transfer/retention in agricultural landscapes, low-order catchments are relevant spatial units because

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in-stream processes and point-source emissions are relatively less important than they are in larger river networks (Burt and Pinay, 2005; Montreuil et al., 2010). Since the 1980s, long-term observatories have been initiated in low-order catchments to identify both the hydrological and biogeochemical process controlling N and P transfer/retention in space and time (Aubert et al., 2013; Neal et al., 2011). These detailed observations of individual catchments have provided scientific understanding, which has served as a basis for the development of process-based models (e.g. Arnold et al., 1998; Beaujouan et al., 2002; Ferrant et al., 2011). However, such models require a large number of input data, which are generally not available for regional-scale assessments (Schoumans et al., 2009).

To determine which landscape features control nutrient diffuse transfer and retention, an alternative approach to process-based modelling consists of considering a large number of catchments, taken as lumped and steady-state entities, and developing statistical approaches (Preston et al., 2011; Tysmans et al., 2013). Models resulting from a statistical approach can be classified into two broad categories: export-coefficient models (e.g. Johnes, 1996; Worrall et al., 2009) and mass-balance models (e.g. Dupas et al., 2013; Grizzetti et al., 2008; Smith et al., 1997). They provide a means to assess water quality in unmonitored catchments and determine the factors controlling it (Kronvang et al., 2003; Wu and Chen, 2013; Zhou et al., 2012). Limits of such models include poor characterisation of agricultural pressures (limited to land-use/land-cover types in the export coefficient approach or N–P inputs in mass-balance models) and ignoring the spatial distribution of catchment attributes.

Additionally, linking N and P loads to the assessment of eutrophication risk in freshwaters is extremely challenging. Many authors consider that development of undesirable non-siliceous algae occurs when N and P levels exceed those of silica (Si), according to Redfield (1958) stoichiometric ratios. According to this view, Billen and Garnier (2007) introduced the Indicator for Coastal Eutrophication Potential (ICEP) to assess the risk of marine eutrophication resulting from excessive nutrient delivery (see also Garnier et al. (2010) and Romero et al. (2013) for applications in coastal catchments worldwide). The ICEP improves the commonly used N:P ratios by considering the stoichiometric C:N:P:Si composition of diatoms, but has never been adapted to freshwater ecosystems.

In this paper, we present an assessment framework which includes: (i) a refined mass-balance model, called Nutting, to estimate diffuse N and P transfer/retention in unmonitored catchments and identify attributes of the catchments controlling them and (ii) a set of indicators to assess the risk of eutrophication resulting from excessive nutrient delivery in freshwater bodies. We hypothesised that we could improve previous mass-balance models by: (i) describing diffuse nutrient sources in terms of soil N surplus and soil P content instead of N and P inputs and (ii) considering catchment attributes not only as lumped variables over the entire area but also within river corridors. Because eutrophication risk is highly dependent on P bioavailability, we tested the sensitivity of the indicators developed to three assumptions about the bioavailability of particulate P. The assessment framework was performed at the country level, and France was chosen as a typical country of Western Europe, with large variability in agricultural pressure intensity and climate conditions.

2. Materials and methods

The assessment framework described in this paper uses monitoring data from 160 independent catchments for calibration. The models developed are then applied to 2210 unmonitored catchments in France. Further description of both calibration and application catchments are given after a presentation of the general methodology.

2.1. Multivariate analysis

A multivariate analysis was performed to relate observed N and P transfer/retention of a set of catchments to spatial attributes describing N and P pressures and the physical environment of the catchment. Hierarchical Clustering on Principal Components (HCPC) combines principal component analysis (PCA), hierarchical clustering (HC) and partitional clustering (specifically *k*-means) (Husson et al., 2010). The PCA consists of projecting nutrient load variables and illustrative variables onto a factorial plan defined by two axes. In HCPC, PCA is a pre-processing step which reduces the number of dimensions in parameter space. In a second step, HC is performed on the PCA axes using Ward's criterion. The number of clusters is chosen visually from the hierarchical tree and is based on the increase of inertia. Finally, the clusters obtained from the hierarchical tree cut are used to initialise the *k*-means algorithm, which 'consolidates' the initial clustering. We performed the HCPC with functions from the R software (R Development Core Team, 2012) package 'FactoMineR'. This clustering method identifies different catchment types based on observed N and P loads in dissolved and particulate forms and relates this typology to the physical environment of the catchments.

2.2. Statistical modelling

2.2.1. Model structure: Nutting-N

Nutting-N (NUTrient Transfer modellING-Nitrogen) is a statistical model that links N sources and catchment land and river attributes to estimate mean annual total-N and nitrate-N loads. The name of the model, Nutting, means that it is constructed from few datasets which cannot completely represent all processes involved in N transport from land to rivers. The foundation of the Nutting-N model is to make the best use of available data at national or regional levels to optimise model accuracy. Total-N and nitrate-N specific loads (TNload and DNload, in $\mathrm{kg\,N\,ha^{-1}\,yr^{-1}}$) at the outlet of each catchment are expressed as:

$$\mathrm{TNload} = R_{TN} * (B_{TN} * \mathrm{Nsurplus} + \mathrm{Npoint}) \tag{1}$$

$$\mathrm{DNload} = R_{DN} * (B_{DN} * \mathrm{Nsurplus} + \mathrm{Npoint}) \tag{2}$$

where Nsurplus is the soil N surplus [$\mathrm{kg\,N\,ha^{-1}\,yr^{-1}}$], Npoint is the sum of all domestic and industrial point sources in the catchment [$\mathrm{kg\,N\,ha^{-1}\,yr^{-1}}$], and R_{TN}/R_{DN} and B_{TN}/B_{DN} are river and catchment transfer factors, respectively. The river and catchment transfer factors express the percentage of the load that is transferred in the terrestrial part and the aquatic part of the catchment. They combine observed variables and calibrated parameters and vary from 0 to 1. In Eq. (1), $R_{TN} * B_{TN} *$ Nsurplus represents the contribution of agricultural diffuse source, and $R_{TN} * B_{TN} *$ Npoint represents the contribution of domestic and industrial point sources to total-N specific load.

In the original description of Nutting-N (Dupas et al., 2013), total runoff was partitioned into a shallow and a deep component to address the issue of catchments that are not at equilibrium, and included a benthic denitrification factor. Here, we considered only one flow component and no benthic denitrification factors in order to reduce the number of parameters in the model. The resulting simplified version of Nutting-N differs from earlier models (e.g. Grizzetti et al., 2008; Smith et al., 1997) because diffuse N sources are characterised by N surplus instead of N input and because the river-transfer factor was inspired by the denitrification function of

Boyer et al. (2006), adapted for lumped application in catchments. The river-transfer factor is calculated as:

$$R_{TN} \text{ or } R_{DN} = \exp\left(-\alpha j * \frac{T}{D}\right) \quad (3)$$

where αj is a mass-transfer coefficient to be calibrated, T is the specific residence time in the river network (s ha^{-1}) and D is the mean stream depth (m).

The catchment transfer factor B is calculated as:

$$B_{TN} \text{ or } B_{DN} = \exp\left(-\sum_i \alpha j * Xi\right) \quad (4)$$

where αi are coefficients to be calibrated and Xi are predictor variables selected from available catchment attributes. These are defined either as lumped variables or within river corridors (see Section 2.4.3). Predictor variables which are expected to have a positive effect on N transfer (e.g. effective rainfall) are entered as their reciprocals, so that all $\alpha i < 0$ and B_{TN}/B_{DN} vary between 0 and 1.

2.2.2. Model structure: Nutting-P

Nutting-P (NUTrient Transfer modellING-Phosphorus) was built similarly to Nutting-N, but diffuse P sources are characterised by the amount of P in the topsoil instead of P surplus. This choice relied on a trial-and-error procedure aiming to minimise the root mean squared error of prediction (RMSEP) with different combinations of candidate variables (Ptopsoil, Ptopsoil × erosion coefficient, P surplus). A benthic retention factor was added because it increased the accuracy of model prediction, unlike in Nutting-N. Total-P and dissolved-P specific loads (TPload and DPload, respectively) at the outlet of each catchment are expressed as:

$$\text{TPload} = (B_{TP} * \text{Ptopsoil} + \text{Ppoint}) - \text{Ret}_{\text{benthic}} \quad (5)$$

$$\text{DPload} = R_{DP} * (B_{TP} * \text{Ptopsoil} + \text{Ppoint}) - \text{Ret}_{\text{benthic}} \quad (6)$$

where Ptopsoil is the amount of P in the 0–0.3 m topsoil [kg P ha^{-1}]; Ppoint is the sum of all point-source emissions in the catchment [kg P ha^{-1} yr^{-1}]; Ret$_{\text{benthic}}$ is a benthic denitrification factor and R_{DP}, B_{DP} and B_{TP} are two river and one catchment transfer factors, respectively. They are computed in the same manner as R_{TN} and B_{TN}. Variables included in the factors B_{DP} and B_{TP} may differ from those in B_{TN} and B_{DN}, however. In Eq. (5), B_{TP} * Ptopsoil represents the contribution of agricultural diffuse source, and Ppoint represents the contribution of domestic and industrial point sources to total-P specific load.

Although the processes involved in long-term retention of dissolved-P in the river system (i.e. adsorption onto particles followed by sedimentation) differ from those involved in N retention (i.e. denitrification), R_{DP} remains a function of the same river geometry variable as R_{TN} and R_{DN} (Eq. (3)). We assumed that dissolved-P retention is a function of the contact time with river sediments and the height of the water column. Ret$_{\text{benthic}}$ is calculated from lakes' hydraulic residence times with the Euroharp nutrient retention tool (Euroharp-Nutret Tier 2; Kronvang et al. (2004)). We estimated lakes' hydraulic residence times with data on lake geometry (Folton and Lavabre, 2006). No river-transfer factor was included in the total-P model because we considered that the antagonistic processes controlling P retention (i.e. adsorption vs. desorption within the river bed, sedimentation vs. transport of sediments, biological uptake vs. release) balance each other on a pluri-annual basis. The only processes causing long-term P retention at equilibrium are overbank floodplain sedimentation and sedimentation in lakes and reservoirs (Demars et al., 2005). We ignored the former due to lack of data with which to estimate it, and the latter is already included in the Ret$_{\text{benthic}}$ factor.

2.2.3. Variable selection and model parameterisation

A wide range of catchment attributes (see Section 2.4.3.) was tested as potential variables to include in Nutting-N and Nutting-P catchment transfer factors B_{TN}, B_{DN}, B_{TP} and B_{DP}. The variable selection procedure aimed to select a limited number of independent variables to optimise model accuracy and avoid over-fitting (Dupas et al., 2013). It had two steps: (i) re-writing a "linearized" version of equations (1), (2), (5), (6) by log-transforming them and ignoring point sources. Variable selection in the "linearized" model was performed according to the Bayesian Information Criterion and parameters were calibrated by minimising a sum of square function. These optimised parameters were used as initial values for the final parameterisation; (ii) final variable selection and parameterisation in a leave-one-out cross-validation to minimise RMSEP. Final parameterisation relied on minimising a weighted least-squared objective function with a modified Gauss–Newton algorithm. Initial parameter values in the B factor were those estimated in the "linearized" model. Initial parameter values in the R factor were chosen to match the in-stream denitrification rate reported by Kronvang et al. (2004).

Additionally, we performed an uncertainty analysis of model parameters and model predictions. We used the R function 'boot' to draw the bootstrap 95% percentile confidence intervals of model parameters and predictions on the basis of 1000 bootstrap replicates.

2.3. The Indicator of Freshwater Eutrophication Potential

The Indicator of Freshwater Eutrophication Potential (IFEP) is an adaptation for freshwaters of the Indicator of Coastal Eutrophication Potential (ICEP) by Billen and Garnier (2007). Both are based on Redfield's (1958) molar C:N:P:Si composition of diatoms, i.e. 106:16:1:20 in marine waters and 106:16:1:40 in freshwaters. The IFEP measures the degree to which N and P concentrations exceed that of Si, assuming that excessive nutrient delivery causes development of undesirable non-siliceous algae instead of diatoms. The IFEP, which is converted into carbon units, can assess N and P independently (N-IFEP, P-IFEP), as follows:

$$\text{N-IFEP} = \left(\frac{\text{TNload}}{14 * 16} - \frac{\text{Siload}}{28 * 40}\right) * 106 * 12 \quad (7)$$

$$\text{P-IFEP} = \left(\frac{\text{TPload}}{31} - \frac{\text{Siload}}{28 * 40}\right) * 106 * 12 \quad (8)$$

where TNload, TPload and Siload are, respectively, the specific loads of total-N, total-P and Si in kg ha^{-1} yr^{-1}. Index values are expressed in kg C ha^{-1} yr^{-1}. A positive value of N-IFEP or P-IFEP indicates that the nutrient in question exceeds Si and that eutrophication may occur; the lower index indicates which nutrient is limiting.

The limiting nutrient can also be determined by comparing the molar N:P ratio to the Redfield N:P ratio of 16. We also analysed the sensitivity of IFEP to three assumptions about P bioavailability by testing three hypotheses: (i) only dissolved-P forms are bioavailable, (ii) dissolved-P + 30% of particulate-P is bioavailable, and (iii) 100% of total-P is bioavailable. The 30% bioavailability of particulate-P was a plausible estimate according to several authors (Dorioz and Trevisan, 2013; Poirier et al., 2012; Sharpley et al., 1992), despite the high variability observed in bioassay experiments.

2.4. The catchment database

2.4.1. Selection criteria

For the multivariate analysis and to calibrate the Nutting models, we established a dataset of 160 independent observation catchments using national public data from French environmental

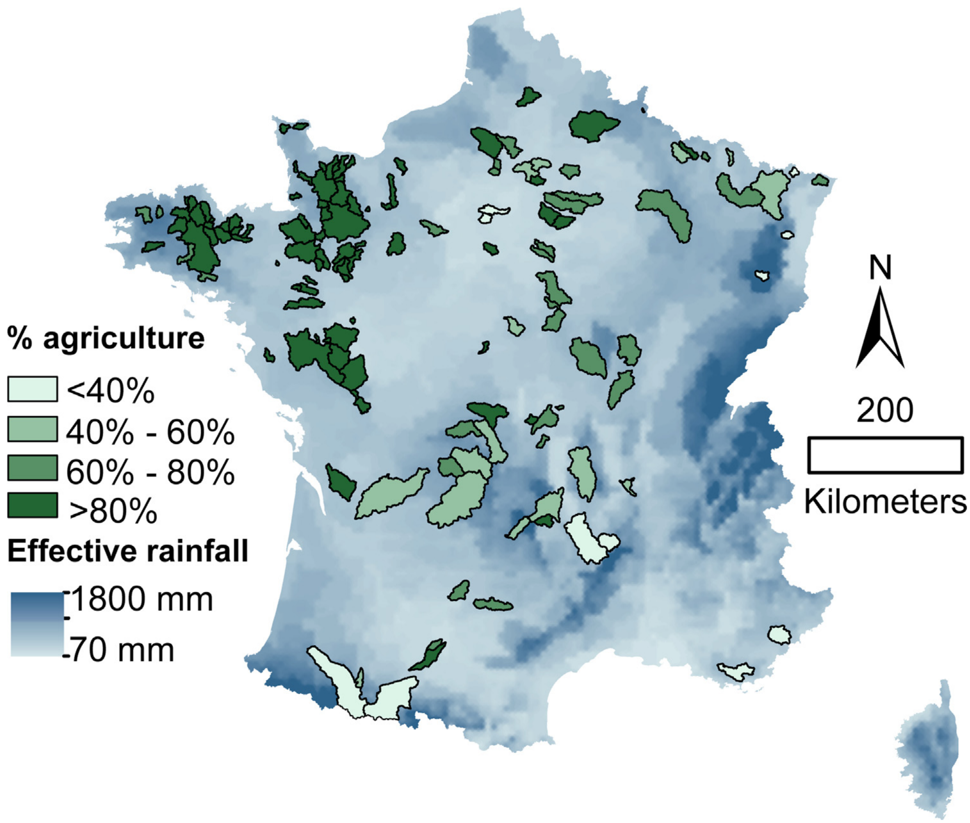

Fig. 1. Percentage of agricultural land use in the 160 catchments selected in France and effective rainfall (Météo France data).

agencies. Catchments were selected based on the ability to estimate mean annual N and P loads for the 2005–2009 period, according to five criteria: (i) presence of water flow and quality stations on the same reach, (ii) ≥1 total-N measurement per month from 2005 to 2009 and ≥100 total-P measurements from 1999 to 2009 to calibrate a rating curve and estimate P load from 2005 to 2009, (iii) <3 missing total-N data points per year, (iv) independence (two nested catchments could not share >20% surface area), and (v) point sources represented <10% of N pressure. Due to difficulties in finding catchments that complied with both N and P criteria, 79 catchments were kept for N- and P-load analysis and 160 for N loads only. Catchment sizes ranged from 10 to 3100 km^2 and cover a wide range of physical and agricultural conditions. Ninety two percent had a Strahler order below 5, but we included 8% of higher-order catchments to increase the variability of river-system size. Mean annual runoff ranged from 70 to 1400 mm and percentage of agricultural land use ranged from 10% to 99% (Fig. 1). Catchment boundaries were delineated with the GeoSAS tool (http://geowww.agrocampus-ouest.fr/web/) using a 50 m DEM.

After calibration, the Nutting models and IFEP indicators were applied to 2210 unmonitored catchments as part of a nation-wide assessment of eutrophication risk. These 2210 unmonitored catchments represent all headwater catchments in the French 'Carthage' database.

2.4.2. Nutrient loads and retention rates

We calculated mean annual specific loads in the 160 observation catchments for the following quality parameters: total-N, nitrate-N, total-P, particulate-P, and dissolved-P. We used water quality data from 2005 to 2009 to remain consistent with the reference years of catchment attributes (Corine Land Cover: 2006, N and P surplus: 2007, point sources: 2007). This time period included wet and dry hydrological years (Gascuel-Odoux et al., 2010; Romero et al., 2013) and was assumed to be short enough to avoid trends in water quality evolution that were not due to interannual climate variability. For N quality variables (total-N and nitrate-N), we used the discharge-weighted concentration method (Moatar and Meybeck, 2007; Moatar et al., 2013) to estimate mean annual loads, i.e. the product of discharge-weighted mean concentration and mean annual discharge. Apparent N retention rate was defined as:

$$\text{Ret N}_{\text{annual}} = 1 - \frac{\text{TNload}}{\text{Nsurplus}} \tag{9}$$

where TNload is the mean annual total-N load [$\text{kg N ha}^{-1}\,\text{yr}^{-1}$] and Nsurplus is the soil N surplus [$\text{kg N ha}^{-1}\,\text{yr}^{-1}$]. N point-source emissions were ignored since they represented a mean (±standard deviation) of only 1.8 ± 9.0% of N surplus.

Total-P load was calculated by summing estimates of dissolved-P load (discharge-weighted concentration method) and particulate-P load (improved rating curve of Delmas et al. (2011)). Among the 160 catchments in the database, we estimated P loads only for 79 due to monitoring that did not meet the previously defined criteria. Annual apparent P retention rate was defined as:

$$\text{Ret P}_{\text{annual}} = 1 - \frac{\text{TPload} - \text{Ppoint}}{\text{Psurplus}} \tag{10}$$

where TPload is the mean annual total-P load in [$\text{kg P ha}^{-1}\,\text{yr}^{-1}$], Psurplus is an estimate of P surplus [$\text{kg P ha}^{-1}\,\text{yr}^{-1}$] and Ppoint is the sum of all point-source emissions of P in the catchment [$\text{kg P ha}^{-1}\,\text{yr}^{-1}$].

Finally, we estimated Si concentrations by considering lithology and base flow index using reference values from Meybeck (1987). Annual Si loads were calculated by multiplying the estimated concentrations by runoff volumes.

Table 1
Catchment attributes and data sources. The last two columns indicate whether the variable was estimated for the entire catchment and/or the river corridor.

Attribute type	Description	Source	Catchment mean	River corridor mean
Diffuse N and P sources	N and P surplus (2007); topsoil P content	Solagro (2010); Delmas et al. (in review)	x	x
N and P point sources	N and P domestic and industrial emissions (2007)	Water agencies	x	
Land use	% artificial surfaces, % agricultural areas, % forest and semi-natural areas, % arable land, % pastures.	Corine Land Cover (2006)	x	x
Soil	Parent material: % Undifferentiated alluvial deposits, % Calcareous rocks, % Clayey materials, % Sandy materials, % Loamy materials,% Detrital formations, % Crystalline rocks and migmatites, % Volcanic rocks; soil texture: % Coarse, % Medium, % Medium fine, % Fine, % Very fine; estimates of hydraulic conductivity and plant-extractable water reserve derived from soil textures using pedotransfer rules of Wosten et al. (2001).	European soil database	x	x
Climate	Effective rainfall, calculated as P-ETP for the months when P-ETP > 0	SAFRAN database, Météo France	x	
Topography, topo-hydrology	Elevation, slope, stream density, topographic wetness index, mean distance to stream	50 m DEM Carthage database Beven and Kirkby (1979)	x	
Connectivity index	Index of Development and Persistence of River networks (IDPR)	Mardhel et al. (2004)	x	x
Catchment size and shape	Catchment size and compacity index (Gravelius)		x	
Stream flow	Annual flow, seasonal flow (four quarters), annual base flow index, seasonal base flow index (four quarters)	French Banque hydro		
River channel geometry	Channel slope, channel depth, channel width, streamflow velocity	ESTIMKART, Pella et al. (2012)	x	
Soil erosion	Annual soil erosion rate	Cerdan et al. (2010)		x

2.4.3. N–P pressure and transfer variables

A total of 110 variables characterising both N–P pressures and transfer risk were estimated for the 160 calibration catchments. Point-source variables included domestic and industrial N and P point-source emissions recorded by public water agencies (pers. comm.) for the 2007 reference year. Diffuse-source variables included estimation of N and P surplus as well as the total-P content in the topsoil. N surplus was calculated by the NOPOLU method (Schoumans et al., 2009; Solagro, 2010) as the sum of agricultural N balance (N inputs–N outputs) and atmospheric deposition. Agricultural N inputs consist of organic/inorganic fertiliser and N fixation; outputs represent the amount of N in harvested crops and grass/fodder. Input and output values were estimated with data from agricultural censuses (e.g., livestock, crops) and crop export coefficients/animal excretion coefficients. NOPOLU disaggregates these statistical agricultural data at administrative levels to the hydrological level using land-cover information. Atmospheric deposition was estimated over the entire area, including non-agricultural land use. Concerning P, an estimate of P surplus at the national level was performed for this study. The methodology was derived from the NOPOLU method, using crop export coefficients and animal excretion coefficients specific to P. Coefficient values used were the same as those of Senthilkumar et al. (2012). Mineral P fertiliser application was estimated by allocating the amount of fertiliser sold in 2005–2007 (statistical trade data) to agricultural areas using land-cover information. Total-P content in the topsoil (0–0.3 m in depth) was estimated with the method of Delmas et al. (in review), to account for P accumulation in soils.

Transfer variables were related to land cover, soil, climate, hydrology, topography, and river-channel geometry (Table 1). The IDPR (Index of Development and Persistence of River networks) connectivity index is a unitless number from 0 to 2000. It is based on comparing a theoretical river network deduced from elevation to the real network: high IDPR values indicate that surface runoff contributes more to water transfer than deep water percolation (Mardhel et al., 2004). In the database, we lumped catchment data into catchment-attribute variables by averaging quantitative variables (e.g. N surplus) according to surface area. Qualitative variables (e.g. land-cover classes) were considered as a percentage of the total surface area. Each variable in the dataset was averaged for the entire catchment and for the surface area in the river corridor, defined as a 200 m-wide zone on both sides of the streams. Soil variables where considered not only as average values in the catchments, but also in interaction with land-use (e.g. variable % sandy soils on arable land use). River corridors and land-cover/soil interactions are known to influence nutrient transfer/retention within catchments (Curie et al., 2011; Mengistu et al., 2014).

3. Results

3.1. N and P transfer/retention

The catchment database displayed high variability in nutrient loads: observed specific loads for total-N ranged from 4 to 59 kg N ha^{-1} yr^{-1} (mean = 18 ± 11 kg N ha^{-1} yr^{-1}) and observed total-P specific loads ranged from 0.1 to 1.4 kg P ha^{-1} yr^{-1} (mean = 0.5 ± 0.3 kg N ha^{-1} yr^{-1}). Nitrate-N was the dominant form of N (mean = 77 ± 14%), whereas P loads were dominated by particulate forms (mean = 65 ± 14%). The particulate-P:total-P load ratio increased with increasing Strahler order of the catchment (Fig. 2) due to biochemical transformation of dissolved-P into particulate-P in the river network. The Nutting-P model empirically integrates the underlying processes in the B_{DP} parameter.

Apparent retentions of N and P differed greatly, i.e. 53 ± 24% of N surplus versus 95 ± 29% of P surplus. Four of the 160 catchments exhibited a negative apparent N retention rate, either due to errors in N surplus or N load estimates or because these catchments were not at equilibrium (i.e. N loads determined by past N surplus stored within the catchment). Twelve out of 79 catchments exhibited apparent P retention rates outside the [0,1] interval, either because estimated P surpluses were negative or because calculated total-P loads exceeded P sources in the catchments.

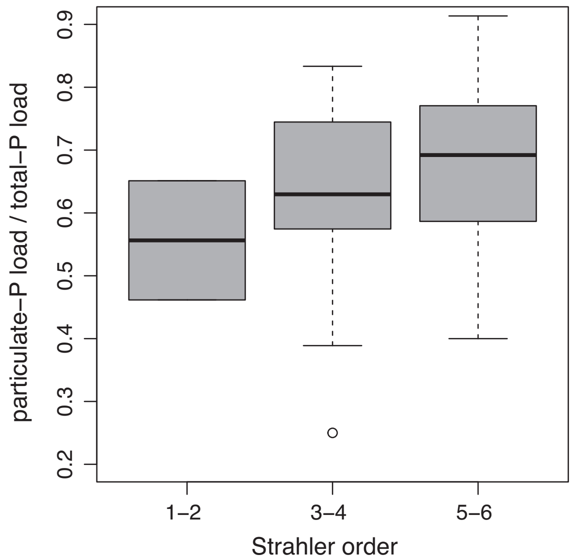

Fig. 2. Boxplots of annual proportion of particulate-P out of total-P in catchments as a function of Strahler order.

3.2. Relations between N and P transfer/retention and catchment attributes

Firstly, relations between N and P transfer/retention and catchment attributes were analysed variable per variable. Observed N loads increased with increasing percentage of agricultural land use (Fig. 3a). Below 60% agricultural land use, annual nitrate-N loads generally remained below 10 kg N ha^{-1} yr^{-1} (mean = 6.4 ± 3.8 kg N ha^{-1} yr^{-1}); above 60% agricultural land use, variability in the nitrate-N loads increased, ranging from 2.5 to 52.0 kg N ha^{-1} yr^{-1} (mean = 16.5 ± 10.2 kg N ha^{-1} yr^{-1}). The large scatter observed for N load when agricultural land use exceeded 60% was refined when considering the N surplus (Fig. 3c); the slope of the TNload = $a \times$ Nsurplus line equals 0.47, which is consistent with the 53% mean apparent retention. Forty eight percent of the variance was explained by this simple regression equation. The annual N retention (i.e. 1 – regression coefficient in Fig. 3c) was a negative function of annual runoff (Fig. 3e).

Such a clear trend was not observed between P loads and percentage of agricultural land use (Fig. 3b). P load is also a positive function of P surplus, but the linear regression fitted to the data explains only 11% of the variance (Fig. 3d). No apparent relation was visible between annual P retention and annual runoff (Fig. 3f).

Secondly, an HCPC multivariate analysis was performed to cluster catchments according to their N–P load features (Fig. 4). According to the PCA, total-N loads were positively correlated with nitrate-N:total-N ratios, i.e. nitrate was the dominant N form in catchments with high N loads. High N loads were associated with high runoff values and high N surplus (Fig. 4a). Total-P loads were negatively correlated with dissolved-P:total-P ratios, i.e. particulate P was the dominant P form in catchments with high P loads. High total-P loads were associated with high runoff and high IDPR values and negatively correlated with the base flow index. Conversely, the dissolved-P:total-P ratio was positively correlated with the base flow index. This suggests that P is mainly transferred to streams as particulate P via superficial runoff pathways in catchments where the connectivity between land and water is high. High IDPR and high runoff values characterise highly connected catchments. The least flashy catchments, characterised by a higher base flow index, had a larger proportion of dissolved-P in the total-P loads but transferred less P. N was transferred to streams mainly as nitrate-N, especially in catchments with high N surplus and high runoff. The IDPR index of surface connectivity was less influential for N than for P, which suggests that N was delivered to streams mainly via base flow transport pathways.

The HCPC resulted in three catchment clusters (Fig. 4b). Cluster 1 included catchments with high N and P loads, a relatively high percentage of nitrate-N and a low percentage of dissolved-P; they had low base-flow indices and high runoff values. Cluster 2 included catchments with low N and P loads and a relatively high percentage of dissolved forms; they had high base-flow indices and low runoff values. Cluster 3 included a greater variety of catchments, characterised by high P loads and low N loads. Hence, catchments can be prone to N or P problems depending on the cluster to which they belong.

3.3. Fate of N and P loads by statistical modelling

3.3.1. Load estimation with the Nutting model

The variables retained by the selection procedure with Nutting further identify which catchment attributes control N and P transfer/retention. Table 2 summarises optimal parameter values, standard errors and 95% bootstrap confidence interval. For the nitrate-N model, the basin transfer factor B_{DN} included effective rainfall and the percentage of forest and semi-natural areas in the catchment. The latter variable, which was not included in the original Nutting-N model (Dupas et al., 2013), reduced RMSEP from 6.3 to 5.9 kg N ha^{-1} yr^{-1}. It corresponds to an R^2 as high as 0.66 for specific nitrate load and 0.84 for global nitrate load estimation in a leave-one-out cross-validation. Bootstrap estimates of nitrate-N load ranged from −10% to +9% of the mean model prediction. For the total-N model, the basin transfer factor B_{TN} included only effective rainfall. R^2 equalled 0.59 for specific total-N load and 0.85 for the global load. Bootstrap estimates of total-N load ranged from −12% to +10% of the mean model prediction.

The basin transfer factors B_{DP} and B_{TP} were a function of the IDPR index for both dissolved-P and total-P models. R^2 equalled 0.45 for the dissolved-P model and 0.40 for the total-P model when predicting specific P load in the leave-one-out cross-validation. This corresponds to an R^2 as high as 0.83 and 0.70 when predicting the global load of dissolved-P and total-P, respectively. Bootstrap estimates of dissolved-P load ranged from −18% to +15% of the mean model prediction. Bootstrap estimates of total-P load ranged from −13% to +12% of the mean model prediction.

The variable selection procedure with Nutting did not result in the inclusion of any ‘spatially-defined’ variables in Nutting-N or -P. This suggests that lumped variables were better predictor variables than those defined within the river corridor or within specific soil types. Application of the Nutting-N and -P models on 2210 headwater catchments allowed us to estimate the contribution of agricultural diffuse emissions to N and P loads (Fig. 5). Diffuse agricultural sources represented 97% of total total-N load, on average, i.e. 12.4 ± 7.1 kg N ha^{-1} yr^{-1}. In contrast, they represented only 46% of total-P load, on average, i.e. 0.31 ± 0.14 kg P ha^{-1} yr^{-1}.

3.3.2. Eutrophication risk

N loads exceeded Si loads in 90% of the 2210 headwater catchments (i.e. N-IFEP > 0), which indicates that P availability generally controls the potential risk of eutrophication related to nutrients. Hence, estimated eutrophication risk was highly sensitive to assumptions about the bioavailability of particulate P. Fig. 6 shows the distribution of min (N-IFEP, P-IFEP), whose value indicates eutrophication risk when it exceeds 0, under three assumptions: when assuming that all P forms were bioavailable, 63% of the catchments were potentially at risk; this percentage dropped to 45% and 26% when assuming that 30% particulate P + dissolved P and only dissolved P forms were bioavailable, respectively. The greater difference in density functions on the right side indicates that

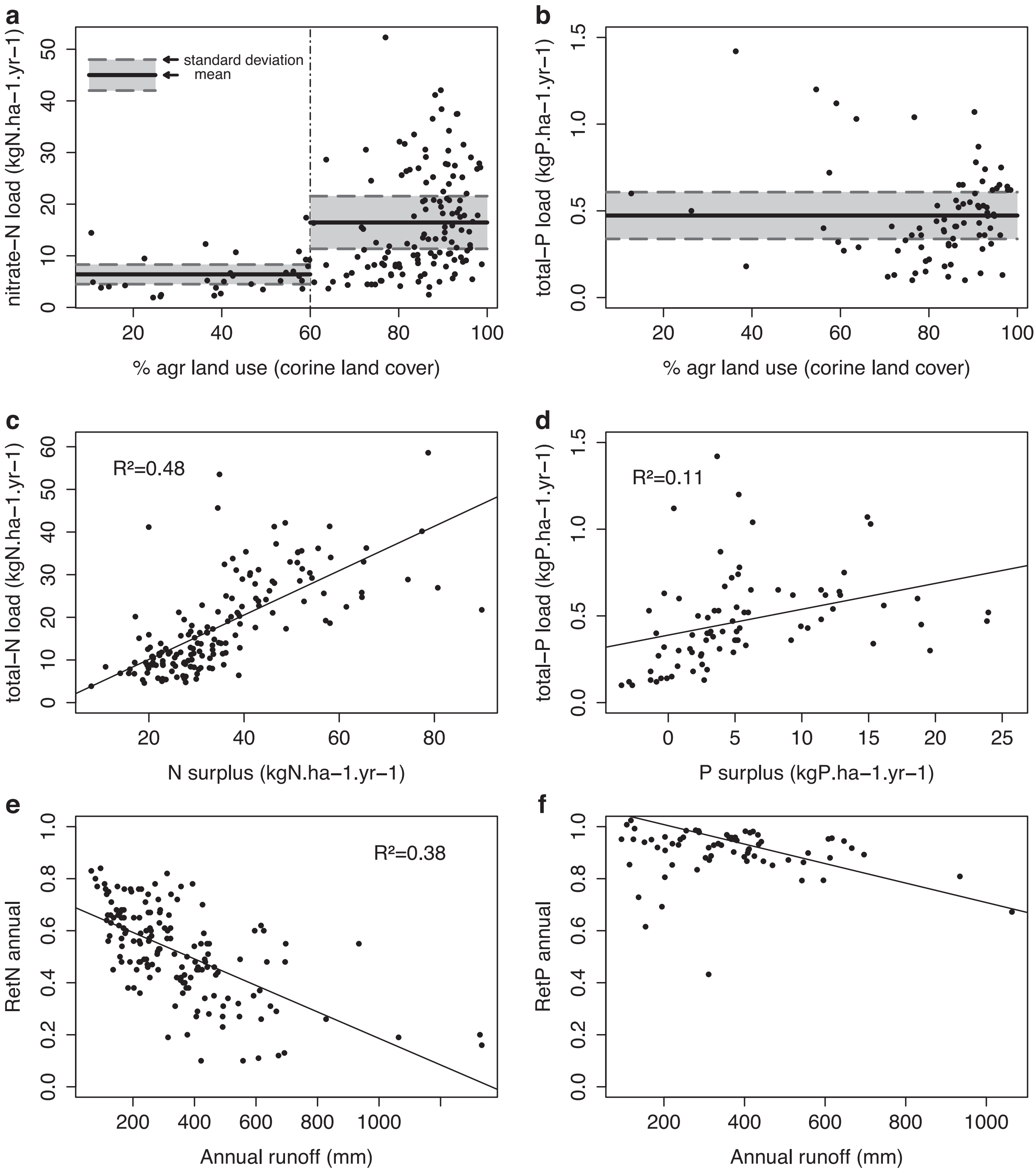

Fig. 3. Nutrient load and apparent retention as a function of catchment attributes: (a, b) land use, (c, d) nutrient surplus and (e, f) annual runoff.

uncertainties about eutrophication risk were highest in catchments with high P loads because they had a high percentage of particulate-P. Thus, they were highly sensitive to the fraction of particulate-P assumed to be bioavailable.

4. Discussion

4.1. Catchment attributes controlling nutrient transfer/retention

Both multivariate analysis and the variable selection procedure with Nutting indicate that N and P loads were more directly related to variables describing agricultural nutrient pressure, i.e. N and P surplus and topsoil P, than to land-use classes. N surplus and topsoil P content are relevant variables for describing agricultural pressures at large scales, provided that enough agricultural and soil data exist to estimate them in some detail (Windolf et al., 2011, 2012). The rate of N transfer is controlled mostly by effective rainfall, as suggested by the relation between annual runoff and apparent N retention rate. P transfer rate was more highly correlated with the IDPR index, a qualitative indicator of connectivity via surface or subsurface runoff. This agrees with the common understanding of N and P transfers: P is transported mostly via

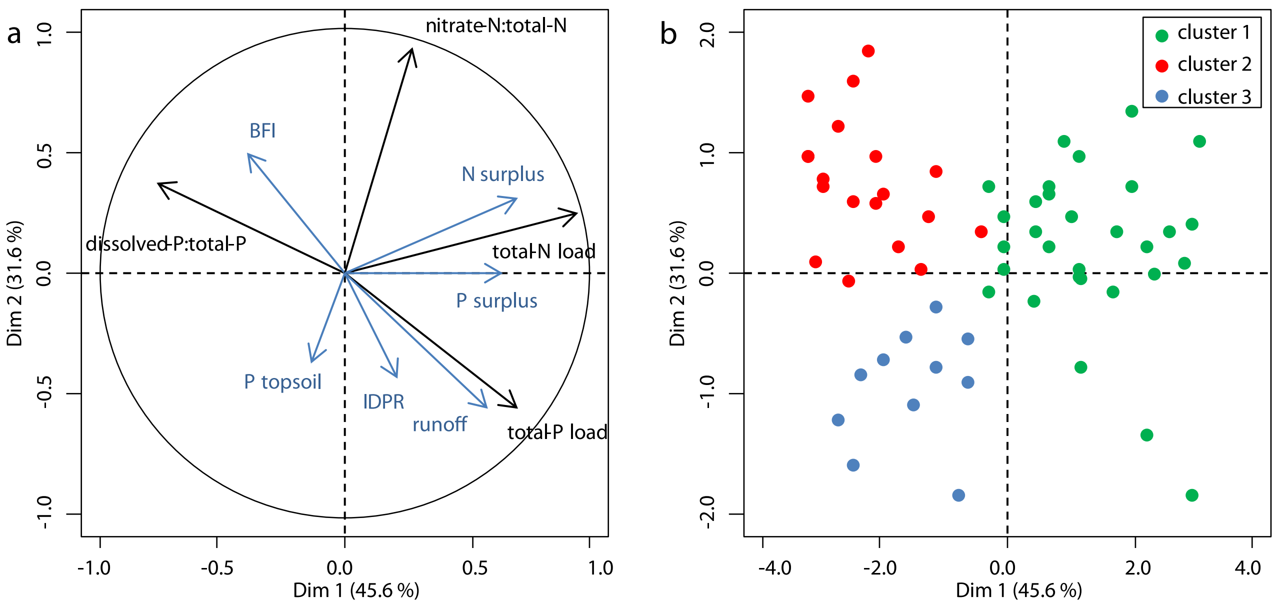

Fig. 4. Hierarchical Clustering on Principal Components (HCPC). (a) Variable factor map with 4 nutrient-load and nutrient-ratio variables (total-N load, total-P load, nitrate-N:total-N ratio, dissolved-P:total-P ratio) projected onto a factorial plan. Illustrative variables (in blue) were projected onto the same factorial plan but did not contribute to construction of the axes. (b) individual/cluster map of the Principal Component Analysis. (For interpretation of reference to color in this figure legend, the reader is referred to the web version of this article.)

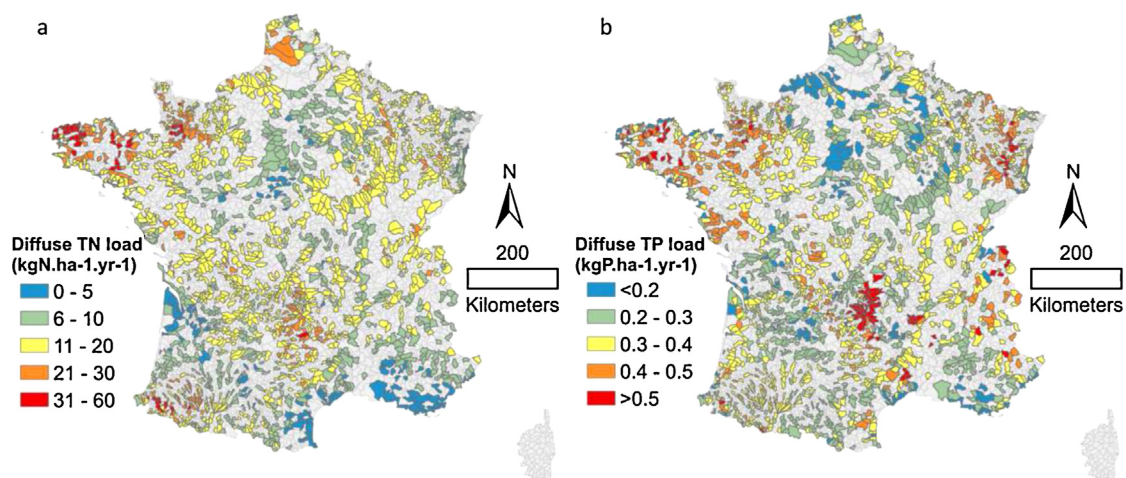

Fig. 5. Application of Nutting models on 2210 headwater catchments of the Carthage database. (a) total-N load of agricultural origin; (b) total-P load of agricultural origin.

surface or subsurface runoff and erosion from a P stock which has accumulated over years in soils; N is transported through annual leaching of N surplus via deeper transport pathways (Mellander et al., 2012; Parn et al., 2012). However, the fact that the proportion of particulate P forms increases with increasing stream order suggests that high particulate-P:total-P load ratios do not result only from erosion dominating P transfer but from stream processes that convert dissolved-P into particulate-P along the stream network

Table 2
Parameter estimates from Nutting-N and Nutting-P models. αi refer to the parameters included in the basin transfer factor and αj refer to the parameter included in the river-transfer factors.

	Model parameters	Units	Estimate	Standard error	*P* value	Bootstrap 95% CI lower bound	Bootstrap 95% CI upper bound
(a) Nutting-nitrate-N	αi (1/effective rainfall)	mm	1.45E+02	3.90E+01	2.72E-04	5.69E+01	2.73E+02
	αi (% forest and semi-natural areas)	–	1.05E−02	2.48E−03	3.53E−05	6.38E−03	1.55E−02
(b) Nutting-total-N	αj	s^{-1} ha m	4.06E-03	9.70E-04	4.82E-05	7.19E-04	5.99E-03
	αi (1/effective rainfall)	mm	1.43E+02	3.59E+01	1.05E-05	6.50E+01	2.47E+02
(c) Nutting-dissolved-P	αj	s^{-1} ha m	3.48E−03	9.55E−04	3.67E−04	7.80E−04	5.34E−03
	αi (1/IDPR)	-	1.22E+03	1.61E+02	6.46E−11	7.96E+02	1.48E+03
(d) Nutting-total-P	αj	s^{-1} ha m	6.17E−03	1.19E−03	1.53E−06	4.20E−03	9.66E−03
	αi (1/IDPR)	–	3.76E+02	6.16E+01	3.74E−08	2.66E+02	4.78E+02

* Index of Development and Persistence of River network.

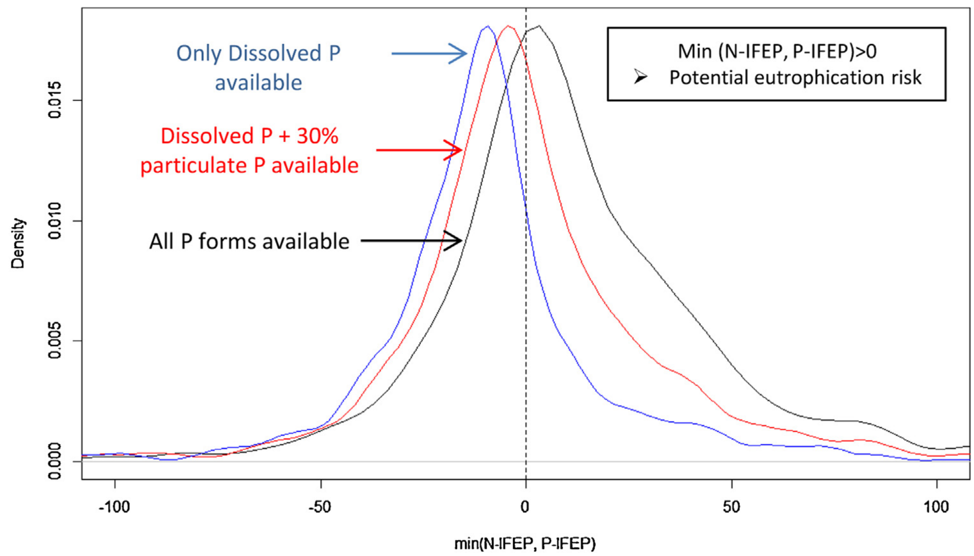

Fig. 6. Density functions of eutrophication risk min(N-IFEP, P-IFEP) in 2210 headwater catchments under 3 hypotheses.

(Kronvang et al., 2012, 2013). In this respect, the present statistical approach generalises the knowledge acquired from process-based studies based on observation of individual catchments.

To our knowledge, this study is the first attempt to consider the spatial organisation of the landscape in a mass-balance model. Whereas all catchment attributes were lumped variables estimated over the entire surface area in previous applications of mass-balance models, we included variables defined within river corridors, such as land use and IDPR. We also attempted to characterise not only average soils in the catchment but also their interaction with agricultural land use. None of these 'spatially-estimated' variables, however, helped to predict nutrient transfers more accurately than the corresponding 'lumped-estimated' variables. Several reasons can explain this negative result: (i) the resolution of national-level GIS datasets is too low for such a spatial approach; (ii) great uncertainties exist in the estimation of catchment attributes that explain most of the variance in nutrient transfer (e.g. N surplus), which prevents identification of the effect of secondary variables; and (iii) the assumption of a steady-state catchment is not correct, which induces imprecision and prevents identification of effects of secondary variables. Previous attempts to include landscape metrics based on proximity to the stream in multiple-regression models of water chemistry generally have not been successful (Jones et al., 2001; Zampella et al., 2007), except that of Johnson et al. (1997), in which attributes defined in upland ecotones explained total-P and suspended sediment loads better than lumped attributes.

The negative result of landscape metrics in Nutting-N and–P might be overcome by: (i) improving estimation and spatial resolution of all variables (e.g. by using recent remote-sensing data), (ii) developing new landscape metrics (e.g. by identifying critical source areas) (Gascuel-Odoux et al., 2011; Heathwaite et al., 2005) or topographic metrics (Creed and Beall, 2009; Mengistu et al., 2014), and (iii) identifying interfaces between source areas and buffer zones. Despite this, the fact that a lumped estimate of N surplus/topsoil P explained most of the variance in N and P loads highlights that reducing nutrient pressures, rather than reorganising agricultural landscapes, is the most powerful mechanism for decreasing nutrient transfer. Nonetheless, spatial organisation of the landscape and buffer zones remain relevant mitigation techniques when considering cost-effectiveness.

Nutting-P was less accurate than Nutting-N with lumped variables, which suggests that landscape connectivity is more crucial for P than for N (Schoumans et al., 2014). The IDPR index was useful for describing hydrology-related connectivity, but landscape-connectivity metrics adapted for a large spatial scale must be created. Potential improvement of Nutting-P may come from adapting distributed suspended sediment models developed for large scales (e.g. Delmas et al., 2009; Van Rompaey et al., 2001; Zhang, 2010).

4.2. Limits of mass-balance models in identifying processes

Mass-balance models such as Nutting are sometimes called hybrid statistical and process-based models because, despite their statistical nature, their structure reflects the understanding of dominant processes controlling nutrient loads. It is thus tempting to use these models to quantify how the apparent retention rate of nutrients is divided between terrestrial and aquatic compartments of catchments. This must be done with caution: equifinality in the calibration of the parameters included in Nutting's *R* and *B* factors might result in inaccurate estimates of the proportion of terrestrial and aquatic retention (Beven, 2006).

Schwarz et al. (2011) have imposed cross-regional constraints on SPARROW parameters to limit their variation between regionally calibrated SPARROW models. By doing so, their regionalised models were consistent with each other but do not ensure consistency with process-based models. In this study, we calibrated Nutting with an iterative algorithm that optimised parameter values to fit the data. As initial parameter values might influence the calibration when the algorithm converges to a local minimum, we chose an initial parameter value in the *R* factor to match the in-stream denitrification rate reported by Kronvang et al. (2004). Finally, the version of Nutting used in this study is more parsimonious than the original (Dupas et al., 2013) to avoid over-parameterisation. One to three calibrated parameters were enough to fit the data in a leave-one-out cross-validation with an R^2 ranging from 0.40 to 0.66 for specific N and P loads and 0.70–0.85 for global N and P loads.

The results of the mass-balance model are based on a steady-state hypothesis, i.e. the assumption of no temporary retention of N and P in any compartment of the catchment during the pluri-annual study period. There has been much discussion about whether some aquifers are temporary N sinks that delay N release or permanent sinks due to denitrification (Van Breemen et al., 2002). The fact that effective rainfall controls a catchment's rate of N transfer may be interpreted as a transit-time effect, which supports the hypothesis of temporary retention, but longer transit time might also result in longer contact times between N and denitrifying conditions, which supports the hypothesis of permanent retention.

Similarly, the hypothesis of steady-state P retention in river systems (i.e. retention and release balancing each other on a pluri-annual basis) is contradicted by budget studies performed on large catchments (Jarvie et al., 2011; Nemery et al., 2005). A P budget performed on the Marne catchment (12,000 km^2) estimated P retention of 15–30% of the total-P input on a pluri-annual basis (Nemery and Garnier, 2007; Nemery et al., 2005). Jarvie et al. (2011), using an extended end-member mixing analysis, estimated 48% retention of total-P in the Sandusky River (3200 km^2) and 14% in the Thames River at Wallingford (3500 km^2). However, the headwater catchments included in our dataset were generally smaller, which led us to ignore permanent retention of total-P through overbank floodplain sedimentation.

4.3. The risk of eutrophication in freshwaters

The IFEP indicators represent a simple way to estimate the potential risk of eutrophication and determine which nutrient limits algal growth, based on 'external' nutrient loadings. The actual functioning of freshwater ecosystems such as lakes is more complex than what could be accounted for in this paper. 'Internal' loadings from anoxic sediments can contribute a large proportion of bioavailable P in lakes and atmospheric fixation by planktonic bacteria can represent a significant source of N (Schindler, 2012). Furthermore, the IFEP used in this study were simplified indicators of nutrient-related potential eutrophication but did not include the effect of other crucial environmental factors, such as light and temperature. Hence, they might fail to predict actual eutrophication, but they remain a useful means for managers to estimate potential eutrophication risk based on nutrient loadings from 'external' anthropogenic sources.

Because national water quality databases generally do not include an estimate of the bioavailable fraction of P on particles, we tested three hypotheses: all P forms bioavailable, dissolved-P + 30% of particulate-P bioavailable, and only dissolved-P bioavailable. We found that estimated eutrophication risk was highly sensitive to these hypotheses. Our recommendation to reduce this uncertainty is to measure P bioavailability in water-quality monitoring programmes, especially in catchments where uncertainty in IFEP results is high. Despite these uncertainties, the IFEP indicators showed that P availability generally controlled eutrophication risk, as N exceeded Si in 90% of headwaters. In this way, our results rather confirm the observations from long-term, whole-system experiments, which have shown that eutrophication in lakes was generally controlled by P availability (Schindler et al., 2008; Schindler, 2012). However, exceptions can exist, as highlighted by the 10% headwater catchments where N was limiting eutrophication. Dual-nutrient reduction strategies can thus be relevant to limit eutrophication in a minority of lakes (Conley et al., 2009). Because the ultimate destination of N and P riverine loads is coastal and marine ecosystems, i.e. N limited ecosystems (Garnier et al., 2010; Howarth and Marino, 2006; Conley et al., 2009), management strategies to reduce both N and P loadings are recommended.

5. Conclusion

We developed a methodology to address the issue of N and P pressure/impact assessment in contexts of scarce data. The methodology consists of (i) a mass-balance model to estimate diffuse N and P transfer/retention and identify the landscape attributes controlling them and (ii) a set of indicators to assess the risk of freshwater eutrophication resulting from excessive nutrient delivery. The Nutting model describes agricultural pressures in greater detail than previous statistical models, thanks to national level data on N and P surplus and P content of the topsoil. No effects of the spatial distribution of agricultural landscapes could be highlighted with this approach. We hypothesised that this was due to inaccurate estimation of variables that explained most of the variability in nutrient loads (e.g. N surplus), which masked the effects of secondary variables. The methodology developed provides a means for river basin district managers to identify the catchments at risk of eutrophication at regional or national level and informs whether nutrient control measures should be directed towards point sources or diffuse sources. Because conclusions drawn from the IFEP indicator were highly sensitive to P availability, we recommend introducing P bioavailability tests in water-quality monitoring programmes, especially when uncertainties in IFEP results are high.

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