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Spatialized N budgets in a large agricultural Mediterranean watershed: high loading and low transfer

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Abstract. Despite the particular management practices and climate characteristics of the Mediterranean regions, the literature dealing with N budgets in large catchments subjected to Mediterranean conditions is scarce. The present study aims to deepen our knowledge on the N cycle within the Ebro River Basin (NE Spain) by means of two different approaches: (1) calculating a global N budget in the Ebro River Basin and (2) calculating a series of detailed regional budgets at higher geographical resolution. N inputs and outputs were spatialized by creating a map based on the most detailed information available. Fluvial and atmospheric N export was estimated together with N retention. The Ebro River Basin annually receives a relatively high amount of new N (5118 kg N km^{-2} y^{-1}), mostly in the form of synthetic fertilizers (50 %). Although it is a highly productive catchment, the net N input as food and feed import is also high (33 %). Only 8 % of this N is finally exported to the delta zone. Several territorial units characterized by different predominant uses (rainfed agriculture, irrigated agriculture and pastures) have differentiated N dynamics. However, due to the high density of irrigation channels and reservoirs that characterize Mediterranean catchments, N retention is very high in all of them (median value, 91 %). These results indicate that problems of eutrophication due to N delivery in the coastal area may not be too severe but that high N retention values may instead lead to problems within the catchment, such as pollution of aquifers and rivers, as well as high atmospheric emissions. The most promising management measures are those devoted to reducing agricultural surpluses through a better balanced N fertilization.

1 Introduction

The global biogeochemical cycle of nitrogen (N) has been deeply altered, and the boundary within which humankind can operate safely has long been crossed (Rockstrom et al., 2009). Approximately 19 Tg N of reactive nitrogen (Nr) annually enter Europe, of which ca. 58 % corresponds to synthetic fertilizers, 18 % to food and feed import, 18 % to industry and vehicle traffic, and 5 % to crop biological fixation (Sutton et al., 2011). Agricultural systems receive the highest Nr inputs and Leip et al. (2011) estimate that only 39 % of applied N finds its way to consumers or is further processed industrially. Excess Nr from different sources generates negative impacts on human health, climate and biodiversity, water, soil, and air quality (Sutton et al., 2011).

During the last few decades, Nr inputs in Spain have evolved differently than in other European countries. Emission and deposition of N oxides (NO_x) and ammonia (NH_3) have decreased in the majority of the EU countries, while in Spain they have increased by 22 % and 18 %, respectively (EEA, 2007; Fagerli and Aas, 2008). Use of synthetic fertilizers in Europe has slightly decreased, while the use of organic N has globally increased, with large regional variations (Oenema et al., 2007). In Spain, however, consumption of N fertilizers has grown despite a slight decline in the surface of land devoted to agriculture (http://faostat.fao.org/). In addition, other intensification indicators have also increased in Spain during the last two decades, including consumption of pesticides, degree of mechanization, amount of irrigated lands and crop productivity (http://faostat.fao.org/). N emission from wastewater has slightly increased in many European countries as well as in Spain (Bouraoui et al., 2011).

Fluvial catchments consist of integrated spatial units pertinent for the study of interactions between humans and the environment. Billen et al. (2011) estimated that about 78 % of the net anthropogenic input of Nr into European catchments is stored or eliminated before reaching the river outlet. The Ebro River Basin (NE Spain) is the largest fluvial catchment in Spain. It covers 17 % of the Spanish Iberian land area and provides a clear example of agricultural intensification under Mediterranean conditions. Many of its streams, from head- to downstream waters, are enriched in nitrate, with this pollution mostly related to agricultural activities (Lassaletta et al., 2010). According to Lassaletta et al. (2009), agriculture accounts for ca. 82 % of the variance of nitrate concentrations in many Ebro basin streams and this influence increased during the 1980–2005 period. In particular, irrigated agriculture can have an important impact on water quality (Causapé et al., 2004; Isidoro and Aragüés, 2007; Arauzo et al., 2011). Many of the aquifers in the catchment, mainly those placed in irrigated agricultural areas, have been polluted by nitrate and have been declared as Nitrate Vulnerable Zones according to the Nitrates Directive (e.g. those placed in the central part of the main axis of the Ebro river or those placed in the area of the confluence between the Cinca and the Segre rivers; http://www.chebro.es).

The scientific literature dealing with N budgets in large river catchments under Mediterranean conditions is scarce and practically absent for Spain. However, the study of the response of N levels to human activities and specifically to agricultural practices in European Mediterranean catchments is of great importance for three reasons: (1) Mediterranean-type ecosystems are present in many parts of the world (Mediterranean basin, California, central Chile, Cape region in South Africa, and areas in South and South-West Australia); (2) ecological processes in Mediterranean-type ecosystems differ greatly from those in other ecosystem types, such as temperate ecosystems; and (3) many global climate change scenarios predict an increase in summer temperatures and a reduction in rainfall together with an increase in the risk of summer droughts in some temperate ecosystems, which would therefore resemble the conditions found in Mediterranean areas (IPCC, 2007; Trnka et al., 2011). Many examples of the particular features of Mediterranean ecosystems exist in the scientific literature within different domains, e.g. plant physiology (González-Fernández et al., 2010), N biogeochemistry (Breiner et al., 2007), limnological and watershed processes (Álvarez-Cobelas et al., 2005; Barceló and Sabater, 2010), impacts of agricultural practices (Zalidis et al., 2002) or N deposition effects (Ochoa-Hueso et al., 2011).

The Ebro River Basin is a typical Mediterranean catchment, with much of its surface subjected to semiarid conditions. A high number of channels and reservoirs that provide the water supply for irrigated agriculture have largely modified the river network. The Water Framework Directive and its River Basin Management Plan (RBMP) are now being implemented in the catchment. Many of the measures currently proposed in the draft of the RBMP are devoted to reducing N pollution. The selection of adequate measures is a crucial item, since their efficacy is frequently much lower than expected (Oenema et al., 2005; Bechmann et al., 2008; Thieu et al., 2010) and because their application requires very large investments (Hutchins et al., 2009; Oenema et al., 2009). Therefore, a detailed study of N budgets, its dynamics, and its transfers within the catchment may be a useful basis to evaluate the potential effectiveness of corrective measures.

In this context, the present study aims to expand the knowledge on the N cycle in the large European Mediterranean catchment of the Ebro River. The specific objectives are: (1) to calculate an overall N budget in the Ebro basin in order to examine the degree of human-induced alteration of the N cycle at the catchment scale, (2) to analyze the effect of reservoirs and irrigation channels on N's fate, assuming that reservoirs and channels have an effect on N retention because they modify the natural flow regime, increase water retention (reservoirs) and imply a redistribution of water within the landscape, and (3) to calculate a series of detailed regional budgets, considering distinct sub-catchments and territorial units, in order to study the contribution of the different N inputs and their transfers at a higher geographical resolution. Finally, the results herein obtained are used to discuss the effectiveness of the different management measures envisaged.

2 Study area

The study area includes the Ebro River Basin (NE Spain), 85 566 km^2, discharging into the western Mediterranean Sea (Fig. 1). The catchment is heterogeneous in terms of geology, topography, and climatology. In general, silicic rocks are located in the uppermost altitudes (3408 m a.s.l. is the highest altitude) while calcareous materials are found at lower elevations (1000–3000 m). The central part of the catchment is a sedimentary and evaporitic Tertiary depression of marine origin with thick layers of gypsum, halite, and other salts.

The topography modulates the Mediterranean climatic patterns throughout the catchment, with a distinct transition from a semiarid environment in the center of the catchment to humid conditions at its northern ranges, influenced by the Pyrenees. The average annual precipitation in the 1920–2002 period was 622 mm, varying from over 950 mm in the west-central Pyrenees to less than 500 mm in the arid interior (Romaní et al., 2010). The fluvial network has a total length of 13 049 km and of 30 255 km when including the smallest streams. The Ebro River discharges 9930 $hm^3 yr^{-1}$

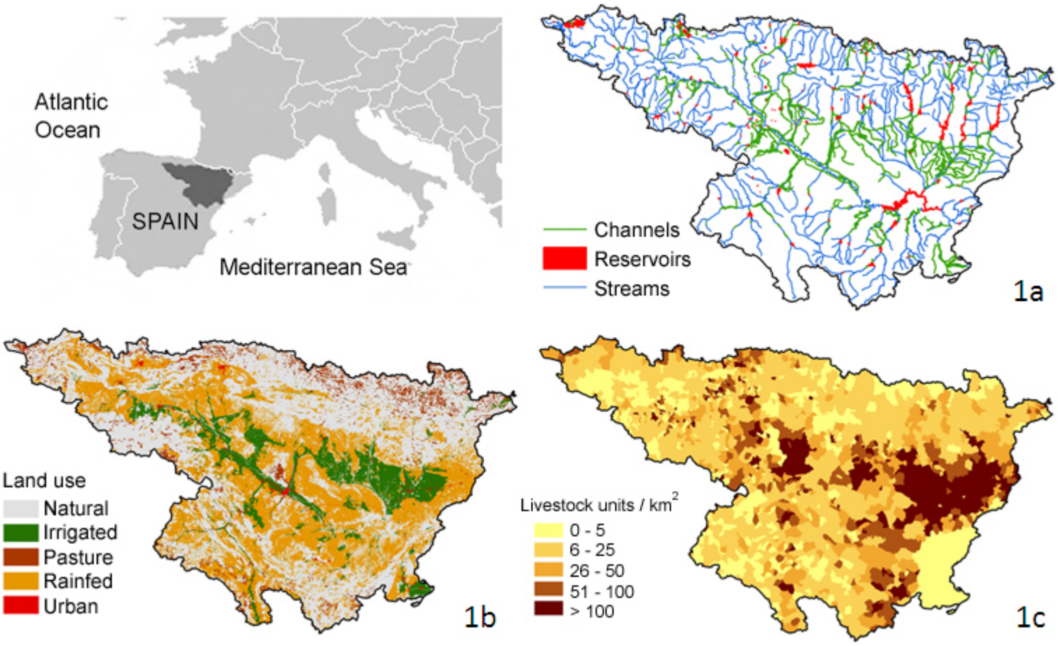

Fig. 1. Study area **(a)** river network, channels and reservoirs; **(b)** land use; **(c)** livestock density.

(2001–2005 average) into the Ebro delta as a seventh-order river, after 910 km of main channel (Fig. 1a).

The agricultural area accounts for 48 % of the total catchment area and about 20 % of that is devoted to irrigated agriculture (information from the map of the European environmental landscape based on interpretation of satellite images, CORINE Land Cover Project) (Fig. 1b). The total water demand is 8190 $hm^3 yr^{-1}$ (i.e. 82 % of total discharge), of which 7681 $hm^3 yr^{-1}$ corresponds to irrigation. The river network has been greatly modified: 109 large reservoirs with 7580 hm^3 total capacity have been constructed to ensure the water supply and to produce electricity; 850 dams are present on the water courses (http://www.chebro.es). Finally, a dense channel network 5139 km in total length is present in the irrigated areas.

About 3 million inhabitants live in the Ebro River Basin, with a population density of ca. 34 inhabitants km^{-2} (less than 50 % of the Spanish mean). Around 45 % of the population is concentrated in five cities with a population over 100 000 inhabitants. A great effort has been made to control the quality of point source effluents in the catchment. The number of wastewater treatment plants increased from 1 to 259 from 1989 to 2005 (Oscoz et al., 2008). As a result, a drastic reduction in the urban input of nutrients has been achieved; in keeping with this, Bouza-Deaño et al. (2008) and Ibáñez et al. (2008) have reported significant reductions in phosphate (PO_4^{-3}) levels during the same period.

3 Material and methods

3.1 Nitrogen budgets

3.1.1 The NANI approach

We have calculated an overall budget for the whole catchment using the Net Anthropogenic Nitrogen Input approach (NANI). This approach has been demonstrated to be a useful tool to study N budgets in large European catchments (Billen et al., 2011) and has been successfully used in many scientific studies (Boyer et al., 2002; Howarth et al., 2006; Schaefer and Alber, 2007; Billen et al., 2009; Schaefer et al. 2009; Howarth et al., 2011). To that purpose, we first estimated the total "new" anthropogenic inputs entering the catchment, that is: synthetic fertilizers, N fixation, net N deposition, and net import of food and feed. Net import of food and feed was estimated by the difference between heterotrophic needs of humans and livestock, and autotrophic production (Billen et al., 2010). For the estimation of net N deposition, contrary to the procedure described by Howarth et al. (2006, 2011) where only the deposition of oxidized N is taken into account considering that reduced N is mostly linked to local redeposition of ammonia volatilization, we here calculated the net deposition of reduced N forms from the balance between emission and deposition provided by the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) at a 50 × 50 km resolution (http://www.emep.int/). Thanks to this approach we can determine whether net reduced forms are entering the catchment from the outside or if, on the contrary, they are being atmospherically exported.

Finally, knowing the N fluxes delivered from the watershed at its outlet into coastal waters, the overall retention/elimination within the whole watershed can be estimated. The term "retention" is used to designate all the processes preventing nitrogen load from being transferred to the outlet of the drainage network, as discussed by e.g. Lepisto et al. (2001) and Billen et al. (2011). This retention thus includes definitive elimination as inert N_2 through denitrification processes, as well as storage in soil, perennial vegetation, groundwater, or sediments. An Index of Coastal Eutrophication Potential (ICEP) based on silica values from the literature (Falco et al., 2010) was calculated as described in Billen and Garnier (2007).

3.1.2 The soil balance approach

Besides the overall NANI approach, we also established a series of detailed budgets for different territorial units and for several sub-catchments (see Sects. 3.3 and 3.4 below) using a soil balance approach (de Vries et al., 2011). To that end, we estimated all the N inputs to agricultural soils, including synthetic fertilizers, biological N fixation, manure application, and total atmospheric N deposition (reduced and oxidized compounds). The difference between these agricultural inputs and the outputs via grazed or harvested crops corresponds to the agricultural surplus, which is the potential source of diffuse pollution to the water and the atmosphere. Adding these surpluses to the N point sources and again taking into account the N river export, the proportion of N "retained" in each of the sub-catchments or territorial units considered was estimated.

3.2 Input-output map

To calculate detailed budgets, we spatialized the N inputs and outputs by creating a GIS database that compiles the most detailed information available on crop yields and crop surfaces for the year 2000. The information was provided by the Spanish Ministry of Agriculture (http://www.mapa.es/). The data are organized by province (which corresponds to the NUTS3 category of the Nomenclature of Territorial Units for Statistics European division) and those that were partially or totally included within the Ebro watershed were selected. Overall, we obtained information on 82 rainfed crops, 86 irrigated crops, 13 greenhouse crops, pastures, and fallow land (Supplement, S1). Information on harvested straw for cereals and legumes and on grazed fallow and stubble is also provided. Productivity of cultivated grasslands and natural pastures was obtained from the Spanish Ministry of the Environment (MMARM, 2010a).

We estimated the mineral inputs for each crop using detailed N fertilization per crop data provided by the European Fertilizer Manufacturers Association (EFMA; http://www.efma.org/); the data were specific for Spain and based on registered consumption figures. In those cases in which a particular crop was not clearly specified, the Spanish fertilization recommendations from MMARM (2010b) were used. Biological N_2 fixation by legumes was estimated through an equation that relates crop yield, N fertilization, and crop residues (Supplement, S2). This equation takes into account the fact that, in the period prior to nodulation, the entire external N is obtained by legumes from mineral nitrogen present in the soil, while only after nodulation is achieved is N progressively assimilated from N_2 fixation. Using this equation, values from the general literature that might overestimate fixation in low productive crops and underestimate it in high-yield crops can be disregarded. Crop N output calculations were based on the N yield of each crop in each province and on the N content of the harvested products (Urbano, 2002; Supplement, S1). The production of fallow and crop residues that are grazed by livestock is provided at the province level by national statistics. These N outputs were also calculated, but they contribute to less than 0.01 % of the total outputs and were therefore considered negligible.

To accurately spatialize the information, we obtained the most detailed layer of CORINE Land Cover project (http://www.epa.ie/whatwedo/assessment/land/corine/), CLC-level 5, for the year 2000 and used the 26 categories comprised in category 2 of the first level (agricultural areas) and those categories belonging to category 3 (natural and semi-natural areas) that correspond to natural and semi-natural pastures. Within the 14 categories of the mixed agricultural type included (CLC 24110–24420), the proportion of each type of use was estimated based on detailed information provided by the Spanish Ministry of Promotion (MF, 2002). First of all, we assigned each crop from the Spanish agricultural statistics to its corresponding category in CLC. Knowing the contribution of each crop to the total (by province) and using the Agricultural Statistics-CLC table of correspondence, we obtained a map including synthetic fertilizer inputs, biological N_2 fixation, and crop outputs (Supplement, S3–S4).

We also gathered detailed information on bovine, ovine, porcine, caprine, equine, rabbit and avian livestock units at the municipal level for the year 2000; overall, they correspond to a total of 3 752 494 livestock units, heterogeneously distributed over the catchment (Fig. 1c). These data were used to estimate N inputs from manure (see details in the next section). Spatialized information on atmospheric N deposition of oxidized and reduced N compounds is available from the EMEP 50×50 km grid. Inputs from the population were estimated using data from the national demographic statistics database (http://www.ine.es), and the inventory of wastewater treatment plants (WWTP) was provided by Confederación Hidrográfica del Ebro CHE (http://www.chebro.es) (Supplemen, S5). The type of wastewater treatment and the number of inhabitant-equivalents were taken into account to estimate the N inflow from WWTP to freshwater streams. In areas with no access to WWTP services, we applied a generic reduction of their N emission adjusted by the proportion of inhabitants connected (0 % reduction) versus non connected (50 % reduction) to collection systems. Industrial emissions, partially included and spatialized in WWTP effluents, were completed with data from the European Pollutant Release and Transfer Register (www.prtr-es.es). Adding all this information to the previous map, we obtained a final map where all N inputs and outputs were spatialized (Fig. 2). It is important to note that even though we attempted to obtain the most accurate spatialized information available, the results cannot account for local specificities and/or particular management practices.

3.3 Territorial units

In order to obtain detailed budget calculations (N inputs, outputs and surpluses), the catchment was divided into different territorial units (TUs) according to their agricultural, livestock, and hydrographic characteristics. To do so, we overlaid the map of main uses (Irrigated and rainfed crops, pastures, natural and urban areas) with the map of livestock units. We defined each TU so as to delimit homogeneous units. The boundaries were then slightly modified to adapt the units to the hydrological features and to the limits of the studied sub-catchments (see next section). Nine TUs were considered, classified into three types. TU 1 (1a, 1b, and 1c) and TU 2 (2a and 2b) have more than 50 % of its territory in agricultural use. The irrigated lands are mostly concentrated in TU 2. The manure application rate is higher in TU 2 than in TU 1. TU 2a has the highest manure application rate and TU 2b the highest population density. In TU 3 (3a, 3b, 3c, and 3d) natural and semi-natural lands predominate. Pasture lands are mainly concentrated in TU 3 and the manure application rate is higher than in TU 1 due to the presence of medium densities of non- or semi-stabled livestock. TU 3 has the lowest population density (Table 1, Fig. 3)

We assumed that all the manure produced in each TU is equally spread over the agricultural areas of this TU and we attributed 85 kg N per Livestock Unit. However, because much of the N coming from stabled livestock does not finally reach crops, we applied the rate proposed for Spain by Oenema et al. (2007), i.e. 80 % of the N in the manure finally reaches the agricultural lands.

3.4 Stream N fluxes, channels, and reservoirs

The mean pluri-annual N flow at the outlet of several nested catchments spread throughout the Ebro basin (Fig. 4) was calculated using daily discharge data and monthly (occasionally bi-monthly) N concentration values from 21 stream monitoring stations of the Water Quality Department

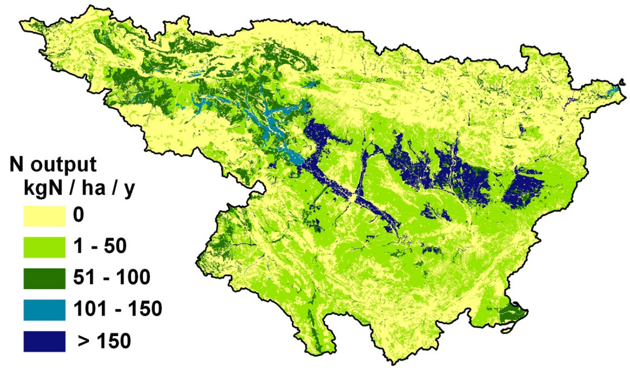

Fig. 2. Spatialized crop N outputs in the Ebro River Basin. Similar maps have been created for all N inputs. Similar maps for the other terms of the N budget are presented in Supplement, S4.

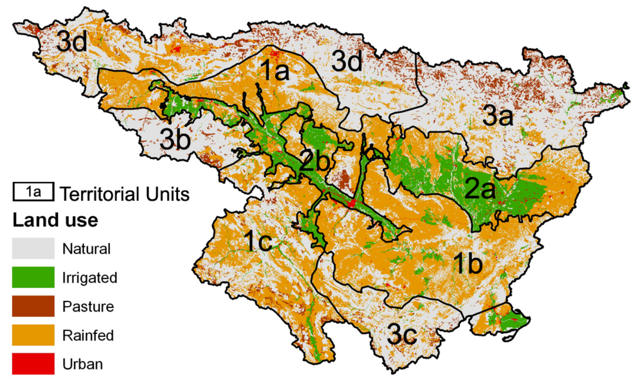

Fig. 3. Territorial units selected to calculate detailed N budgets.

of the Ebro Basin Confederation. We have included all sites with enough information to estimate N flows (Supplement, S6). Only information on dissolved inorganic nitrogen (NO_3^-, NO_2^-, NH_4^+) was available and we estimated total N applying the equation described in Garnier et al. (2010) to take into account dissolved organic nitrogen. When possible, we used data from the 1995–2005 period to calculate the pluri-annual mean. A “soil balance approach” budget was calculated as well as the N retention in these 21 sub-catchments.

In addition, the density of irrigation channels was calculated in each sub-catchment, expressed in km km^{-2}, and the fraction of surface area in the catchment that drains into a dam reservoir was expressed as a percentage. The effect of these two variables on N retention was statistically analyzed. First of all, we correlated the surface area of the catchment that drained into a dam with the percentage of retention by means of a Spearman Rank Order correlation. Secondly, we split the data into two groups: samples with a proportion of surface higher or lower than 0.058 km km^{-2}; this value corresponds to the irrigation density of the whole Ebro basin. We compared the mean retention of these

Table 1. Characteristics of the nine territorial units.

Territorial Unit	Surface km^2	Agricultural land (%)	Rainfed agriculture (%)	Irrigated agriculture (%)	Pastures (%)	Natural and semi-natural (%)	Urban (%)	Livestock units	KgN manure ha^{-1} agriculture	Inhab km^{-2}
1a	9412	68	65	2	2	31	1	217 771	26	70
1b	14 122	67	63	4	0	32	1	529 295	43	33
1c	11 080	57	49	4	4	43	1	246 100	29	17
2a	8495	83	41	42	0	16	2	1 628 842	164	45
2b	5557	86	26	60	0	10	4	352 435	51	92
3a	11 745	25	9	2	13	75	0	274 206	68	6
3b	3836	20	11	2	7	80	0	55 219	55	13
3c	5105	30	24	1	4	70	0	161 489	77	6
3d	14 127	28	18	1	9	71	1	283 512	53	28

two groups performing a Mann-Whitney U-test. Finally, we constructed a non-linear regression model to assess the response of each sub-catchment in terms of % retention with regard to the proportion of surface area that drained into a dam. We used the GraphPad Prism v5.01 (GraphPad Software, Inc.) software to estimate the parameters of the model and also the % of variance explained.

Using the resulting relationships, the overall N retention in each Territorial Unit was calculated from the distribution of dams and the density of irrigation channels. This information, along with the information on N inputs and outputs in each TU, was finally summarized in a diagram where all territorial units and their intra- and inter-fluxes are represented.

4 Results and discussion

4.1 NANI budget in the whole Ebro River Basin

Synthetic fertilizers are the main new anthropogenic N input at the scale of the Ebro catchment, accounting for almost 50 % of the total (2529 kg N km^{-2} y^{-1}). N fixation contributes 15 % (748 kg N km^{-2} y^{-1}). Although the Ebro watershed is a highly productive territory, with about 50 % of its surface devoted to agriculture, there is a large net import of N in the form of food and feed (1689 kg N km^{-2} y^{-1}), accounting for approximately 33 % of the total. The contribution of atmospheric exchanges to the nitrogen budget was calculated from the balance of emissions and deposition of nitrogen compounds as reported by EMEP (http://www.emep.int/). Deposition of oxidized nitrogen (mostly originating from high temperature combustion by traffic and electric generation) accounts for 364 kg N km^{-2} y^{-1}, i.e. 7 % of the net anthropogenic input of new nitrogen to the catchment. On the other hand, emission of reduced nitrogen forms surpasses deposition by 212 kg N km^{-2} y^{-1}, indicating that the Ebro basin exports reactive nitrogen through atmospheric transport, for about 4 % of total anthropogenic inputs.

Yearly, 5118 kg N km^{-2} y^{-1} of reactive nitrogen enters the catchment, an amount somewhat above the European mean (3700 kg N km^{-2} y^{-1}; Billen et al., 2011). However, only 394 kg N km^{-2} y^{-1} finally reaches the Ebro delta through riverine transport. This implies that 92 % of the anthropogenic N inputs are being retained or eliminated inside the catchment. This is a very high retention rate compared with other European catchments from temperate climates, where the retention range is between 50 % and 82 %. At the coast, N inputs lead to a positive ICEP-N value (ca. 4 kg C km^{-2} d^{-1}), an indicator based on the difference between the nitrogen and silica fluxes converted into carbon using the Redfield ratio C:N:P:Si). The eutrophication risk associated to this value is, however, moderate and might also depend on the availability of other nutrients. In this regard, the progressive control of P load over the past two decades (Torrecilla et al., 2005; Ibañez et al., 2008) has lowered the eutrophication potential of the receiving coastal waters. This situation is very different from that observed in other European seas, where high N and P excesses associated with river inflows (with ICEP-N values as high as 30 kg C km^{-2} d^{-1}) are the source of several undesirable effects (e.g. Cugier et al., 2005; Lancelot et al., 2007; Billen et al., 2011).

4.2 N budgets in the territorial units

According to the soil balance approach, the annual N input in TU type 1 (characterized by predominant rainfed agriculture and low livestock densities) is relatively high (4361–6368 kg N km^{-2} y^{-1}). The main input corresponds in all cases to synthetic fertilizers followed by manure application (Table 2), the contribution of biological N_2 fixation, N deposition and point sources being much lower. In TU type 2 (characterized by a high proportion of irrigated agriculture and medium or high livestock densities), the annual N input is very high (22 869 and

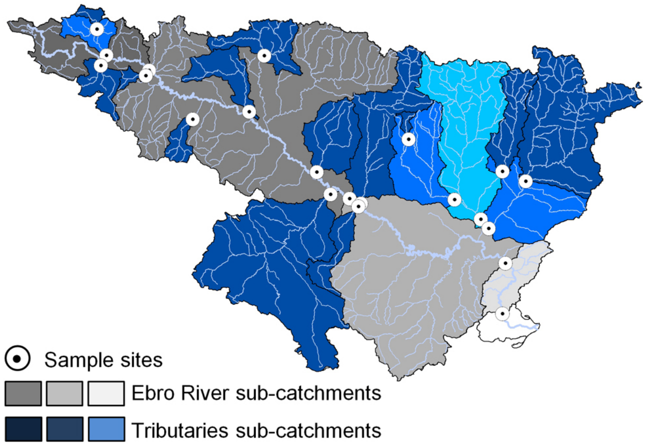

Fig. 4. Nested sub-catchments and the respective stream sampling sites used to estimate pluri-annual N export and detailed N budgets.

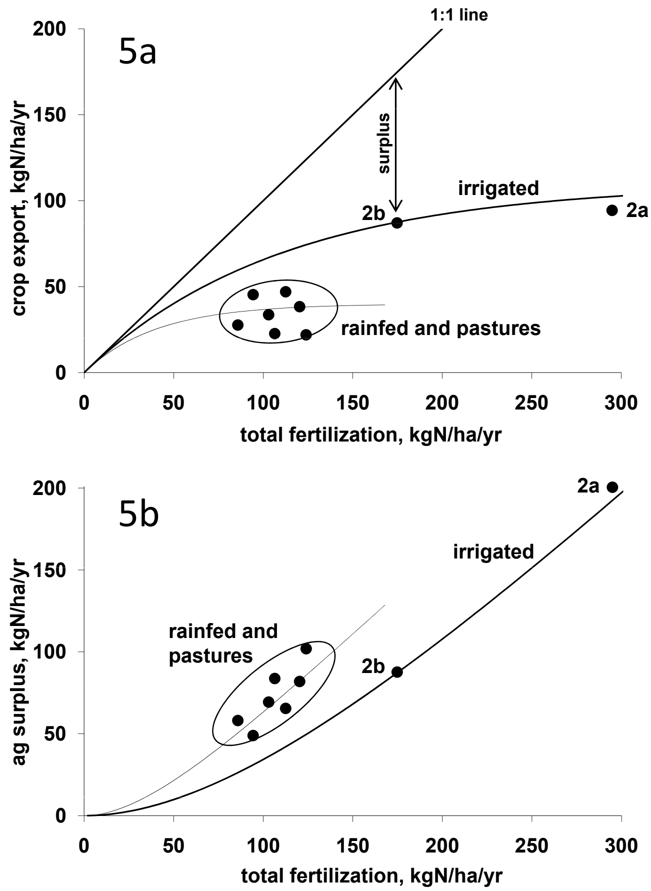

Fig. 5. **(a)** Relationship between total fertilization and crop export. The single parameter relationship $y = Y_{max}$ $(1\text{-}e^{-x/Y_{max}})$ (where y is crop export and x total fertilization) has been fitted to the observations. **(b)** Corresponding relationship between total fertilization and agricultural surplus (surplus is defined as total fertilization minus crop export). Note: territorial units 2a and 2b are those with a higher proportion of irrigated crops (see Table 1).

14 798 kg N km^{-2} y^{-1} for 2a and 2b, respectively). In unit 2a, where the highest livestock densities are found, manure application is the main N input, contributing 55 % of the total. It is remarkable that in units 2a and 2b the amount of N_2 fixed by crops is very high, and accounts for 17–22 % of the total. This is related to the intensive cultivation of N_2-fixing fodder crops such as alfalfa. Total inputs in TU type 3 (characterized by low agricultural surfaces and a high proportion of pasturelands) are the lowest in all cases (1832–3405 kg N km^{-2} y^{-1}). In all these units, the main input corresponds to manure followed by synthetic fertilizer application. In all units, the contribution of point sources is very low, not higher than 6 % of the total.

Figure 5a shows the relationship between agricultural N output from agricultural soils (crop N yield) and the corresponding total N agricultural inputs (synthetic fertilizer, manure, N_2 fixation, and N deposition) for agricultural land in each TU. The pattern of irrigated territories is very different from that of rainfed and pasture lands. Irrigated crops have no water limitation and consequently the threshold at which they do not respond to new N additions is higher than that of rainfed crops and pastures. In both cases, however, a threshold is reached above which all extra N applied directly produces a surplus instead of an increase in productivity. Figure 5b shows how surpluses increase with increasing inputs. TU 2 makes up most of the irrigated agriculture that produces very high N surpluses. These TUs are located over the majority of areas that have been declared as Nitrate Vulnerable Zones (http://www.chebro.es). In TU 2a, characterized by very high livestock density, the agricultural surpluses are the highest. It is in this area where many of the historical increasing trends in nitrate stream concentration have been observed (Lassaletta et al., 2009). The non-point source N pollution is not an exclusive problem of irrigated agriculture, however, and TUs characterized by rainfed agriculture can also present high agricultural surpluses. These results are coherent with the N stream levels and export observed in previous studies in small rainfed sub-catchment within the Ebro catchment (Lassaletta, 2007; Lassaletta et al., 2010).

4.2.1 N transfers within the Ebro River Basin

We calculated the N retention in a set of 21 sub-catchments distributed throughout the Ebro basin. Except for one small catchment, retention was always above 45 % and the values were generally very high (median, 91 %). The Spearman rank order correlation shows a significant relationship between the surface area of the catchment drained into a dam reservoir and the percentage of retention ($R = 0.59$; $p = 0.004$).

Table 2. Nitrogen inputs and outputs in the territorial units (kg N km^{-2} y^{-1}) (The figures in brackets are the % of each input to the total inputs for each TU).

Territorial Unit	Total input	Synthetic Fertilizer	Manure	N-Fixation	N Deposition	Point Sources	Output	Agric. Surplus
1a	5975	3363 (56 %)	1545 (26 %)	153 (3 %)	532 (9 %)	381 (6 %)	2691	2903
1b	6378	2918 (46 %)	2473 (39 %)	241 (4 %)	518 (8 %)	228 (4 %)	1310	4839
1c	4361	2420 (56 %)	1461 (34 %)	115 (3 %)	319 (7 %)	46 (1 %)	1394	2921
2a	22 869	5243 (23 %)	12 624 (55 %)	3989 (17 %)	843 (4 %)	171 (1 %)	7266	15 432
2b	14 798	6175 (42 %)	4123 (28 %)	3251 (22 %)	590 (4 %)	658 (4 %)	7048	7092
3a	2734	711 (26 %)	1531 (56 %)	210 (8 %)	254 (9 %)	29 (1 %)	863	1843
3b	1832	663 (36 %)	958 (52 %)	37 (2 %)	133 (7 %)	40 (2 %)	585	1206
3c	3405	1034 (30 %)	2100 (62 %)	47 (1 %)	206 (6 %)	18 (1 %)	601	2786
3d	2887	1132 (39 %)	1308 (45 %)	90 (3 %)	247 (9 %)	111 (4 %)	1160	1616

The retention was significantly higher (M-W $U = 26$; $p = 0.046$) in the group that comprised catchments with a large density of irrigation channels (>0.058 km km^{-2}). In these irrigated catchments, retention was invariably high, 92 % on average. The p value is, however, close to the critical alpha value ($\alpha = 0.05$) due to a certain overlap between two samples in the upper range of the data set. Non-irrigated catchments (density of irrigation channels <0.058 km km^{-2}) present a very wide range of retention values (Fig. 6). In these catchments, the percentage of retention is also highly controlled by the surface area of the catchment drained into a dam. We adjusted these data using the following relationship (Fig. 7):

$$\%\,\text{Retention} = 95 - Ae^{(-D\omega^{-1})} \quad (1)$$

where D is the % area "controlled" by a dam
A is set to 55 %
ω is set to 16 %

The R^2 of this model is 0.57 and therefore explains nearly 60 % of the variance in the retention. Inland water masses such as lakes, ponds, and reservoirs were recognized as N retention and processing hotspots (Garnier et al. 1999, 2000; Passy et al., 2011). Lepistö et al. (2006) found a similar relationship between the fraction of surfaces covered by lakes and the percentage of N retention in catchments in Finland. The maximum retention found by these authors is, however, much lower than that found in the Ebro sub-catchments.

Using the above relationships and taking into account the distribution of dams and the density of irrigation channels in each Territorial Unit, we calculated their overall N retention (Table 3). All this information together with that obtained in the soil N balance is summarized in a diagram where all territorial units and their intra- and inter fluxes have been represented (Fig. 8).

The main inputs are produced in units 2a, 1b, and 2b. Even though agriculture in unit 1b is less intensive than in unit 2b, its total contribution is higher due to a higher agricultural surface. In general, retention in all units is very high and this means that little N is transferred to downstream units. The lowest retention was estimated for TU 1c, where both the channel density and the surface area of the catchment drained into a dam are the lowest. Retention in this TU is 80 % and it is the only one with a value comparable to those estimated for European temperate catchments (Billen et al., 2011). In TU 2a, even though few dams control the fluvial flows, a very high density of irrigation channels is responsible for high retention values. This means that in this unit, a large proportion of the N entering the unit remains there and can produce many undesirable effects such as eutrophication of surface water, atmospheric emissions, denitrification accompanied by N_2O emissions and/or groundwater pollution. Overall, these results explain the high general "retention" observed in the Ebro catchment.

Intra-annual N export is very different for rainfed and for irrigated crops. In rainfed catchments, N river export closely follows the Mediterranean flow regime and the highest export occurs in winter and early spring, at the time when fertilization takes place, precipitation is higher, and plant nitrogen uptake is lower (Bellos et al., 2004; Moreno et al., 2006; Lassaletta, 2007; Fig. 9). This fluvial N export will be finally retained in a downstream dam where the water is accumulated to supply spring and summer consumption. On the contrary, in those catchments characterized by irrigated agriculture, the water flow regime is modified to guarantee water supply in late spring and summer. This produces an alteration of the N export pattern, which is also high in the summer period, coinciding with crops fertilization and irrigation (Torrecilla et al., 2005) (Fig. 9).

Olesen et al. (2007) have shown how some irrigated agricultural systems in USA acted as net N sinks instead of sources. Despite our results show that a large part of N inputs

Table 3. Characteristics of the territorial units related to their overall hydrosystem N retention .

Territorial Unit	Surface area km^2	Irrigation channel density $km\,km^{-2}$	Fraction reservoirs %	N retention %
1a	9446	0.07	11	92
1b	14 248	0.07	67	92
1c	11 110	0.03	20	80
2a	8542	0.18	29	92
2b	5640	0.33	94	92
3a	11 844	0.03	91	95
3b	3843	0.02	33	88
3c	5113	0.01	76	94
3d	14 252	0.03	63	94

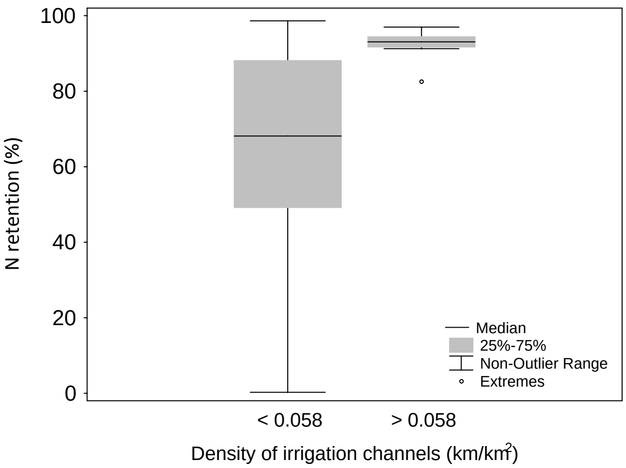

Fig. 6. Distribution of N retention in slightly and highly channelized sub-catchments.

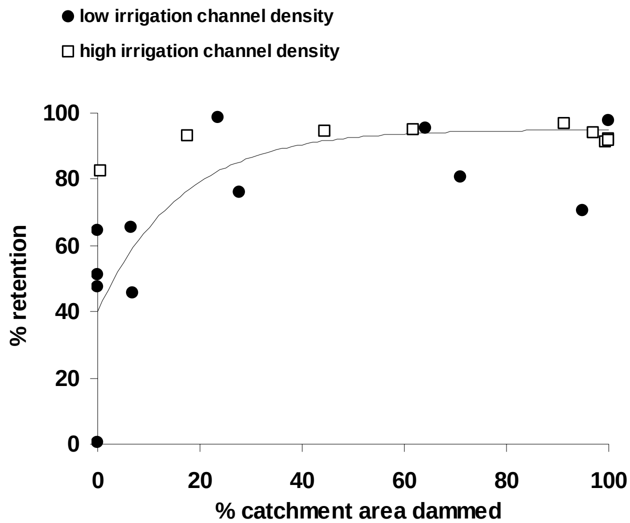

Fig. 7. Calculated retention for 21 sub-catchments in the Ebro basin plotted against the percentage of basin area drained into a reservoir. Catchments with high irrigation channel density (i.e. $>0.058\,km\,km^{-2}$) are represented as open squares.

is being retained within the catchment, this is not the case for the Ebro, where nitrate concentrations have historically increased in many streams (the increase being mainly related to agriculture, Lassaletta et al., 2009) and where nitrate concentrations in the irrigation return flows are also very high (Causapé et al., 2006). Bartoli et al. (2011) have recently underlined the severe effects of the morphological modifications of Mediterranean river networks, like the alterations made to a medium-sized agricultural and highly-channelized Mediterranean catchment in Italy. These authors have found a very high retention in the channels network due to denitrification, which is higher than river retention, and that can account for 12 % of the N surpluses retained in the catchment. High retention rates in channelized agricultural systems, however, can be related not only to the channels themselves but also to the landscapes associated with irrigation practices. Frequent water recirculation on the landscape before reaching the river outlet indeed allows this water to reach the aquifers earlier. Irrigated landscapes also comprise plenty of irrigation ponds (10 000 in the Ebro Basin; www.chebro.es) where N can be processed and retained. Extraction wells are placed in some irrigated areas and some barriers are commonly placed in the streams to divert the water to the channels that could also contribute to water recirculation and N retention, respectively.

We have seen how N fluxes in irrigated systems can be also high in summer (Fig. 9). N retention in rivers is higher during the summer period because high temperatures stimulate N assimilation by the river biota (Merseburger et al., 2005), as well as denitrification (Piña-Ochoa and Álvarez-Cobelas, 2006; Schaefer and Alber, 2007). N export from irrigated

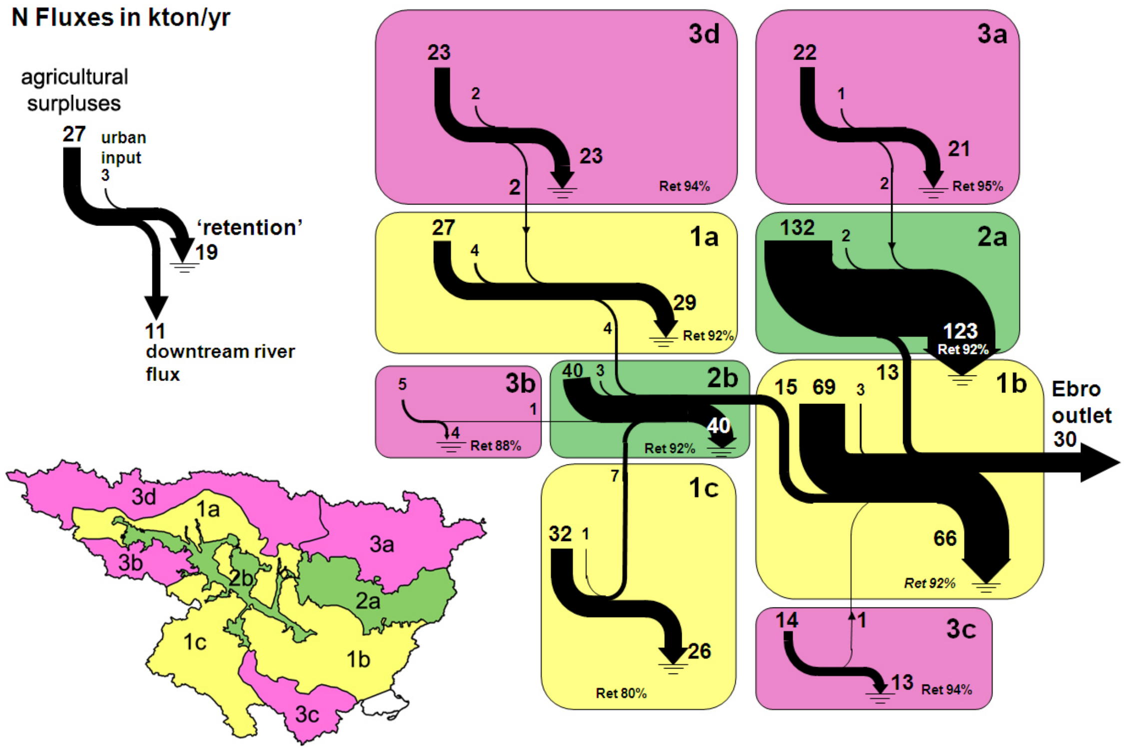

Fig. 8. Schematic diagram of the inter- and intra-territorial units N fluxes.

lands to the rivers and channels has therefore a greater opportunity to be retained or eliminated in the summer period. Finally, the effect of climate on the proportion of N exported by temperate rivers (Schaefer et al., 2009; Howarth et al., 2011) could be exacerbated by the more arid conditions of Mediterranean catchments. Indeed, part of the difference in the retention values observed among sub-catchments may be related to local characteristics such as climatic particularities.

4.3 Management implications

The N dynamics observed in the Ebro catchment are highly controlled by the characteristic land management of Mediterranean catchments. High N retention and assimilation within the catchment produces lower impacts in the sea and generates, in general, fewer eutrophication problems than in Northern European seas. Ludwig et al. (2010) predict a stabilization or even a slight reduction of the Ebro N and P export to the sea in different future scenarios. In this case, the moderate to low risk of coastal eutrophication described in this paper would remain in coming years. This situation produces, however, a high N residence time within the catchment that generates the observed N pollution of streams and aquifers. Chronic accumulation of N in soils and aquifers could imply that

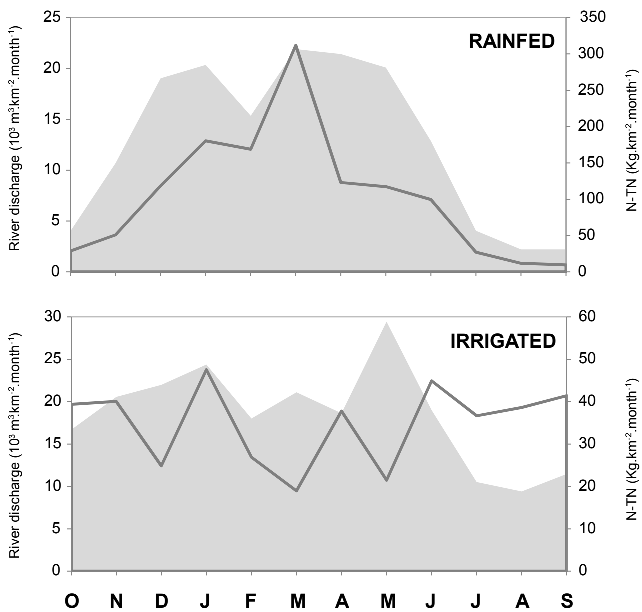

Fig. 9. Annual flow regime and N export in a rainfed and an irrigated catchment. Shaded areas represent river discharge and lines illustrate N fluxes.

N surpluses would be continuously exported for years even after the application of programs aimed at controlling N pollution (Cherry et al., 2008; Tisseuil et al., 2008).

On the other hand, N processing in rivers has been widely recognized as an important way to reduce N pollution problems (von Schiller et al., 2009; Racchetti et al., 2011) because this implies an increase in the amount of N that is being denitrified, therefore shortcutting the N cascade. This process, however, is associated with the emission of nitrous oxide. An increase in N concentrations in the river may not produce an increase in N_2/N_2O yield, but it may produce an increase in the net N_2O emitted (Beaulieu et al., 2011). Indirect N_2O emissions in temperate regions can account for a significant fraction of total agricultural N_2O emissions (Garnier et al., 2009). These indirect emissions in the Mediterranean agricultural landscapes could be even higher. Laini et al. (2011) have recently reported one of the highest N_2O emission observed in aquatic environments in lowland springs within an intensive agricultural catchment of the Po River Basin. Finally, nitrate accumulation in aquifers can also be a source of N_2O emissions (Weymann et al., 2008).

The River Basin Management Plan of the Ebro River Basin is a very ambitious plan that includes many measures devoted to preventing N pollution at local and regional scales, such as modernization of irrigation systems, organic waste management, improvement of fertilization programs, application of codes of good agricultural practices, and the application of specific action plans in those areas declared as Nitrate Vulnerable Zones. From an integrated and sustainable perspective, and considering the results of this work, the most efficient measures would be those devoted to reducing N inputs to the catchment, always taking into account the issue of N swapping between environmental compartments (Grizzetti et al., 2011). It is particularly important to reduce N agricultural surpluses in two ways: reducing N agricultural losses or improving nitrogen use efficiency. Figure 5 suggests that reducing N inputs to agricultural soils could significantly reduce N surpluses with only a limited effect on agricultural productivity. Therefore, among the most promising measures recognized at the EU level (Oenema et al., 2009) balanced fertilization is likely the most appropriate. Due to the high amount of N that annually enters the catchment in the form of food and feed, the use of locally produced and low-protein animal feed (Oenema et al., 2009) would also be an adequate measure.

5 Conclusions

The Ebro River Catchment annually receives $5118\,\mathrm{kg\,N\,km^{-2}\,y^{-1}}$ new N, with synthetic fertilizer application the main N input (ca. 50 % of the total). Although it is a highly productive catchment, there is a net import of N in the form of food and feed (33 % of the total). In some cases, livestock inputs result in a significant N input. Different territorial management practices produce very different dynamics within the N cycle. The hydrological and agricultural management characteristics of the catchment, along with common agricultural practices in Mediterranean areas, namely the high density of irrigation channels and reservoirs, produce high N retention within the territorial units and hamper N transfer among them. As a consequence, very little of the reactive N that enters the catchment flows out to the sea. This prevents severe eutrophication problems in the coastal area but leads instead to many problems in the catchment, such as pollution of aquifers and rivers, as well as high atmospheric emissions. About 30 % of the atmospheric emissions are exported outside the catchment. The most promising management measures are those attempting to reduce agricultural N surpluses by better balancing N fertilization.

Supplementary material related to this article is available online at: http://www.biogeosciences.net/9/57/2012/ bg-9-57-2012-supplement.pdf.

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