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Nutrient export to an Eastern Atlantic coastal zone: first modeling and nitrogen mass balance

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Abstract:

We have studied 15 catchments supplying freshwater to a French Atlantic coastal lagoon, where increase in nitrogen loads due to agriculture is supposed to have destabilized the ecosystem in the last decades. The catchment is a lowland composed of Pleistocene sands with an average slope of 0.25%. To study the nutrient export in relation to land-use surface waters were sampled bi-weekly between October 2006 and January 2009 and land-use was established by plane photographs and Geographic Information System (GIS). Cultivated pine forests represent more than 80% of the total surface and 7% of the catchment area has been deforested recently. Significant areas of some catchments are used for maize crop. Housing is confined to the coastal zone. Maize and forest crop give a robust signature in terms of nitrate export. In view of modeling the nutrient fluxes, we have established the mean export rate for every land-use: forested parcels, deforested parcels, cultivated surfaces, and housing areas export 45, 93, 2850, and 61 kg N-nitrate km^{-2} $year^{-1}$, respectively. Exports of ammonium, dissolved organic N (DON), and dissolved inorganic P (DIP) could not be related to land use. The mean export is 13, 100, and 0.57 kg km^{-2} $year^{-1}$ for N-ammonium, DON, and DIP, respectively. The modeling of nitrogen flux is in good agreement with our measures for the largest catchment, which supplies about 90% of the total continental DIN flux. However, small catchments are more dynamic due to hydrological conditions and the model is less accurate. This work has permitted to complete and unify scattered studies about nutrient cycling in this area. Thus we have established and compared the nitrogen budget of cornfields and cultivated pine forest. We have emphasized that (i) fertilizer use should be reduced in cornfields because they stock between 200 and 6400 kg DIN km^{-2} $year^{-1}$, and (ii) the nitrogen budget in pine forest mostly depends on tree harvesting and symbiotic N-fixation, which is poorly constrained. Export of N by rivers represents a small contribution to the N budget of soils.

Keywords: Nitrogen – Phosphorus – River export – Land use – Coastal catchment – Arcachon Bay – Modeling – Mass balance

Introduction

Littoral ecosystems such as lagoons and salt marshes are some of the most productive environments of the global ocean (Falkowski et al. *1998*). Coastal areas represent 40% of total ocean biologic production, whereas they represent only 10% of oceanic area (Mantoura et al. *1991*). They are powerful biogeochemical reactors and the inner reactions may have global consequences on carbon and major nutrient cycle. About 87% of the Earth's land surface is connected to the ocean by rivers (Ludwig and Probst *1998*) and as a consequence, littoral ecosystems receive continental waters, which may be impacted by human activities, and sometimes severely polluted (Billen et al. *2007*; Meybeck and Helmer *1989*). Anthropogenic inputs of biologically available N and P into terrestrial landscape in the form of artificial fertilizers through cultivation of N fixing crops, via fossil fuel burning, and waste water have caused the accumulation of excess nutrients in continental ecosystems. One of the common

disturbances is eutrophication, which is defined as the enrichment of waters with plant nutrients, mainly phosphorus and nitrogen (Meybeck & Helmer 1989), primarily nitrogen in marine ecosystems (Howarth & Marino 2006). The trophic imbalance provokes an ecological feedback (Howarth 2008; Smith 2003), such as plant growth, which results in visible blooms (floating algal mats) and potential toxic microalgae development (Conley et al. 1993). Decomposition of plant material leads to depletion of oxygen and subsequently fish mortality and decrease in pH. As a global consequence, biodiversity is always reduced because of eutrophication (Galloway 2003). A recent work has shown that the number of hypoxic zones in the coastal margins is doubling every decade (Diaz & Rosenberg 2008).

Shallow coastal bays and lagoons are highly sensitive to eutrophication because they are particularly vulnerable to the rapid changes in population and land use occurring in the coastal zone (Duarte 1995; Nixon et al. 2001; Valiela et al. 1998). Moreover they are important sites for human activities, such as tourism, food resources production (oysters, mussels, clams, shrimps, fishes, salt), and waste dumping, which make these environments vulnerable. Some of these uses are not compatible. The objective of sustainable management is to derive benefits from such exploitations, without affecting the long-term quality of the environment. In this view, several studies have been performed about the larger French coastal lagoon (Arcachon Bay) and its catchment. It was established that the increase in intensive agriculture and nitrogen fertilizer use might destabilize the Arcachon Bay ecosystem (Auby et al. 1994) and macroalgae proliferations was observed during the eighties. Moreover a recent study has highlighted the regression of *Zostera noltii* meadows (Plus et al. 2010) even though these meadows buffer the nutrient loads and limit the eutrophication risk of the Arcachon Bay (De Wit et al. 2001). As a consequence it was necessary to update the nutrient budget originating from continent.

The first purpose of this study was to obtain for the first time and for the entire catchment the nutrient budget and land-use data. In this view we have studied the dissolved organic and inorganic forms of nitrogen and phosphorus of 15 catchments. We have compared the obtained budget with previous ones (e.g. Auby et al. 1994) in order to rely the evolution of the nutrient supply with the eutrophication history of the Arcachon Bay. Secondly, we aim to establish a model of nutrient export based on land-use. The third objective was to compile several partial studies concerning the nitrogen cycle in the Arcachon Bay catchment. This review permitted to establish the nitrogen mass balance in cultivated pine forests and cornfields in order to discuss the sustainability of this cultivation.

1

Studied site

3   The Arcachon Bay (44°40'N, 01°10'W) is a 156-km^2 lagoon located in the French
4   Atlantic coast. The tide amplitude oscillates between 1.1 and 4.9 m. The internal part of the
5   basin emerges at low tide (115 km^2). The intertidal zone covers 66% of the surface area. It
6   encloses the largest seagrass meadow of *Zostera noltii* in Europe (Auby & Labourg 1996).
7   The catchments are a typical lowland, with an average slope of 0.25%. The catchment has a
8   surface of 3001 km^2 and is drained by the Leyre River and by 15 small streams, which are
9   direct tributaries to the lagoon. The geology of the Arcachon Bay catchment consists of an
10   uniform quaternary sand cover (Legigan 1979). The aquifer is a multi-layered system, highly
11   connected. The shallow phreatic aquifer is called the "Sable des Landes". The water table is
12   not deeper than 3 m and the total thickness does not exceed 25 m. It is formed by a
13   homogeneous sand formation. Its bottom consists of a sandy clay layer. Despite high
14   hydraulic conductivity of sands, the groundwater velocity is less than 50 m year^{-1}, because of
15   the small slope between 2 and 4‰ (Rimmelin 1998; Saint Pe 1966).
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Methods

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Catchment boundaries, soil occupation, and river discharge

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22   Catchments studied have been delimited and detailed by Laplana et al. (Laplana et al.
23   1992). Soil occupation has been determined by remote sensing using map of the French
24   institute IGN and aerial photographs analyzed with the Geographic Information System (GIS)
25   ArcGIS.
26   The daily water discharge of the Leyre River is provided by the French public institute
27   of regional environment (DIREN). The discharge is measured at a gauging station with an
28   automatic lymnimeter. We use the product of the Leyre River specific discharge by the
29   surface area of the other streams to estimate their discharge. This extrapolation technique can
30   lead to a large error when geology and slope of the catchment change, which is not the case
31   here. The average slope is about 0.25 % and the catchment and the aquifer are constituted by

a homogenous and thick sand formation (Legigan 1979). Comparison of the extrapolation techniques with real flow measurement made on two rivers (Leyre and Tagon) in 2005 gave good results. The flow of small rivers could be overestimated by about 30% at the annual scale. Flood and low water level are more dynamic in small catchments and badly estimated by interpolation. However for our study it is a sufficient approximation, because the cumulative flow of all the small rivers represents 22 % of the Leyre River flow.

Sampling

We have studied the 15 streams of the Arcachon Bay catchment. The sampling stations were located near the river mouth but upstream the dynamic estuary to exclude marine influences. The sampling frequency was at least two samplings per month and up to four samplings per month in the three main streams (Leyre, Cires and Milieu). This choice permits to have a proper representation of meteorological events and seasonal contrasts linked to soil occupation in farming catchments. The year 2007 was a complete sampling year, and 2008 was limited to the nine major streams. The sampling provided a continuous series to study annual flows. In addition, the French institutes SIBA and IFREMER supplied data of the Leyre quality from a survey between 1971 and 2008 (Auby et al., 1994 and unpublished data). The sampling frequency was two samplings per month. For inorganic nutrient determination two 12 ml samples were collected near the riverbank using a 50 ml syringe and samples were filtered in situ with 0.20 µm cellulose acetate syringe filters. Filtered samples were stored in polypropylene tubes in darkness at -18°C for a few days before analyses. Samples for organic nutrient determination were filtered on GFF filters and stored in glass tubes at -18°C.

We collected 58 samples of rainwater after each precipitation event during 2008. Rainwaters collector was an opaque bottle fitted with a funnel. Rain waters were collected within few hours after rains using a 50 ml syringe and were filtered with 0.20 µm cellulose acetate syringe filters. Moreover three meteorological stations of Meteofrance covering the entire catchment provided data regarding the daily amount of rainfalls. We used the average of the three stations.

1   *Nutrient analysis*

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4   The dissolved inorganic compounds were analyzed colorimetrically for river water

5 and rainwater samples according to standardized techniques. Dissolved nitrates ($\Sigma NO_3^- = NO_3^-$

6 $+ NO_2^-$) were analyzed by Flow Injection Analysis (FIA) according to Anderson (1979).

7 Precision was ±10% for ΣNO_3^-. Dissolved phosphate (DIP) and ammonium were measured by

8 colorimetric procedures (Mullin & Riley 1955; Murphy & Riley 1962; Strickland & Parsons

9 1972). The precision for these methods was ±5% for DIP and 10% for NH_4^+. Total dissolved

10 nitrogen (TDN) and phosphorus (TDP) were respectively measured as ΣNO_3^- and DIP after

11 total oxidation by persulfate reagent according to Valderrama (1981). Dissolved organic

12 nitrogen (DON) and phosphorus (DOP) are the difference between TDN and DIN, and

13 between TDP and DIP, respectively. The error in DON is as high as ±20 % because it

14 corresponds to the difference of two values that can be close. The error in DOP may be

15 higher; the values are indicative and are treated as such. Total dissolved N and P were

16 measured on river water samples only.

17

18   *Annual mean concentrations and annual nutrient fluxes*

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21   The annual streamwater flux (Q_m) is an arithmetic mean of the daily streamwater

22 discharge. The annual flux of nutrients supplied by rivers (F_S) is estimated using commonly

23 applied equations (Meybeck & Ragu 1997; Walling & Webb 1985). First, we calculated the

24 average annual concentration (C_m):

25      $C_m = \sum (C_i . Q_i) / \sum Q_i$

26

27

28 where C_i is the nutrient concentration at time i and Q_i is the streamwater flow at time i.

29 Then,

30    $F_s = C_m . Q_{tot}$

31 where Q_{tot} is the total streamwater discharge during one year.

1

2   We calculated the annual flow of nutrient supplied by rainfalls (F_R) with the same methods

3   substituting the streamwater flow Q_i and Q_{tot} by the rainfalls (P).

4

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6   *Calculation of the export rate*

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8   Export rates are defined according to the land use and average annual flux. The export

9   rate E_i due to the land use i is calculated with the relation

10

$$E_i = F_i / S_i$$

11   where F_i is the average annual flux due to the land use i and S_i is the surface area of the land

12   use i.

13   Since the catchments are heterogeneous, we must progress by stages. First, the nutrient

14   export rate due to forest is calculated from the Aiguemorte catchment because it contains 90%

15   of pine forests, only 3.3% of deforested parcel and no farming area. Secondly, the nutrient

16   export rate due to deforested areas is calculated from the Cassy catchment, which has a

17   significant part of deforested areas (19.3 %), no farming, and very few housing areas. For that

18   we have subtracted the nutrient flux due to forest parcels and we have considered that the

19   remaining flux is due to deforested parcels. Similarly, we have calculated the nutrient export

20   rate due to farming parcels by subtracting from deforested and forest nutrient export rate in

21   mixed land use catchments i.e. for Leyre, Cires, Milieu, and Passaduy. The nutrient export

22   rate due to urban area was calculated from the La Teste catchment because it contains 59.8 %

23   of urban area and few farming area.

24   Based on these average export rates, we computed the DIN flux (F_c) defined as

25   $$F_c = \sum (S_i . E_i),$$

26   where S_i is the mean surface of the parcel i and E_i is the DIN export rate of the parcel i.

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29   *Nitrogen mass balance budget*

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1   The mass balance budget enables to synthesize scattered data about nitrogen

2 biogeochemistry. Moreover it permits to compare the nitrogen cycle in the both ecosystems,

3 cultivated pine forest and cornfields. The N cycle in agro-ecosystems depends on numerous

4 processes; however, it can be simplified according to Galloway (1998; 2003) and Puckett

5 (1999) as: (i) assimilation of DIN from fertilizer, manure, and atmospheric deposition into

6 biomass; (ii) decomposition or mineralization of biomass to ammonium through

7 ammonification and oxidation of ammonium to nitrate through nitrification; (iii) reduction of

8 nitrate to N gas (N_2) through denitrification; (iv) conversion of N gas to ammonium by N

9 fixing organisms through N fixation; (v) loss of ammoniac either to the atmosphere by

10 volatilization; (vi) retention of ammonium on cation exchange sites or in clay interlayers; (vii)

11 removal of N in harvested crops and animals; (viii) loss of DIN to ground water and river by

12 leaching and run-off; and (ix) alteration of mineral.

13   This mass balance is based on data acquired during our survey and data from

14 literature. Inputs of nitrogen due to fertilizer and atmospheric deposition (i) are well known.

15 Atmospheric deposition is provided by the rainwater survey of the present study and the

16 fertilizer use is provided by the French institute of agriculture (AGRESTE). No local data

17 exist about ammonification and nitrification (ii) in these catchments. In the studied zone,

18 maize is cultivated for grain and the both stems and leaves stay in situ after corn harvesting.

19 We consider that this biomass is bioavailable and it is mineralized during the next year and

20 then we estimate the biomass of stems and leaves. The total biomass of cornfield is estimated

21 by the French institute of agriculture (AGRESTE 2000) and Plénet and Lemaire (1999). Sixty

22 % of nitrogen in maize plant is located in grain and 40 % in stems and leaves (Lemaire,

23 personal communication). In a pine forest environment, we consider that ammonification and

24 nitrification are negligible because vegetation is highly limited under mature pine forestry and

25 pine needles are highly depleted in nitrogen. However, this simplification cannot be applied in

26 deforested areas because ammonification of logging residues is high. In that case Loustau et

27 al. (1999) have estimated the amount of nitrogen in barks. Denitrification (iii) in groundwater

28 under cornfields has been studied by Rimmelin (1998) and De Wit et al (2005) and the mass

29 balance budget is based on these data. We suppose that denitrification in forest is negligible

30 due to unfavorable environment: low nitrate concentration (Loustau et al. 1999), and low

31 labile organic carbon (De Wit et al. 2005). Moreover, denitrification is highly limited in sandy

32 aquifer (Groffman & Tiedje 1989). Symbiotic and non-symbiotic fixation of nitrogen (iv) has

33 not been studied in this area. Cornfields do not permit high nitrogen fixation, hence we assess

34 the fixation rate from literature in similar environments. In pine forests of the studied

1   catchments, a significant symbiotic fixation is due to gorse *Ulex europaeus*. We can use a first

2   assessment based on estimated biomass and the natural ^{15}N abundance method in gorse

3   (Augusto et al. 2005). Jambert et al. (1997) have studied the volatilization (v) in cornfields

4   and pine forest (Jambert et al. 1994) with chambers techniques; we use these data. We

5   consider that sorption (vi) is negligible in both ecosystems because the cationic exchange

6   capacity of soils is very low, estimated close to 1 meq (Canton et al. 2010). Assessment of

7   nitrogen loss due to harvesting (vii) is based on previous studies. Loustau et al. (1999) have

8   studied pine harvesting and Plénet and Lemaire (1999) have studied maize harvesting. Loss of

9   DIN due to leaching (viii) was estimated in the present study. We consider that mineral

10   alteration (ix) is not a source of nitrogen because soils contains more than 90 % of quartz

11   (Legigan 1979).

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14   **Results**

15

16   *Land use*

17

18   Pine forests (*Pinus pinaster*) dominate the land use. They occupy more than 80% of

19   the total surface (Fig. 1). Freshly deforested areas represent 7% of the land use (Fig. 1; Tab.

20   1). Intensive farming covers significant areas of some catchments. Housing is rather confined

21   to the coastal zone except in the Leyre region (Fig. 1; Tab. 1). Aiguemorte catchment is

22   dominated by forest (89.5 %) and contains a few deforested areas (3.3 %) and no farming

23   areas. It defines the export rate of forested parcels. Cassy catchment has a significant part of

24   newly deforested areas (19.3 %) and no farming areas. It defines the difference between the

25   export rate of deforested parcels and that of forested parcels. Several catchments (Cires,

26   Leyre, Milieu, and Passaduy) have a significant portion of farming areas and a few housing

27   and deforested areas. They can characterize the export rate of farming parcel by difference

28   with the previous export rates. About 70% of the farming areas are made up of cornfields.

29   Vegetable and flower fields occupy about 30% of farming surfaces (AGRESTE 2000). The

30   Ponteil River catchment is dominated by forestry and is characterized by the presence of a 0.4

31   km^2 domestic waste landfill.

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1

Nutrient concentrations and fluxes

3

The Table 2 summarizes the annual mean concentration in stream water for the 15-stutied catchments. The mean concentration mask the variability of sampling. The standard deviation of nitrate concentrations is included between 30 and 80 % for the overall stations but the major part is included between 40 and 60%. Mean nitrate concentrations are between 0.11 and 2.70 mg N l^{-1} in 2007, and 0.06 and 4.82 mg N l^{-1} in 2008. Ammonium concentrations are less heterogeneous and less variable. Mean ammonium concentrations are included between 0.04 and 0.19 mg N l^{-1} in 2007, and 0.06 and 0.10 mg N l^{-1} in 2008. The Ponteil River is an exception with 2.45 mg N l^{-1} in 2007 and 1.10 mg N l^{-1} in 2008. Mean DON concentrations are between 0.07 and 0.64 mg N l^{-1} in 2007 but the major part of rivers is included between 0.24 and 0.36 mg N l^{-1}. DIP concentrations are very low between 0.002 and 0.009 mg P l^{-1}. The La Teste River is an exception with 0.026 mg P l^{-1}.

The water discharge to the Arcachon Bay of the Leyre River was 467 10^6 m^3 in the year 2007 and 426 10^6 m^3 in 2008. The discharge reached a maximum value of 65 m^3 s^{-1} during winter 2007 and a minimum of 8 m^3 s^{-1} during summer 2007. Nutrient fluxes were calculated for the years 2007 and 2008 and are summarized in Table 3. The total DIN flux is estimated to 836 x 10^3 kg N in 2007 and 969 x 10^3 kg N in 2008, the DON flux is estimated to 174 x 10^3 kg N in 2007 and the DIP flux is 4.8 x 10^3 kg P in 2007 and 2.9 x 10^3 kg P in 2008. The largest catchment that drains the Leyre River dominates overall in fluxes (90 % of the total DIN flux) and water discharge (78 % of the total water discharge). However, small catchments present specific fluxes. Catchments with farming areas (Cires, Milieu, Passaduy, Lanton, Renet) export much more nitrate than non-farming catchments (Aiguemorte, Tagon) despite similar water discharge. Nitrate is the main form of DIN and represents between 80 and 98% of DIN (Tab. 3) except in the Ponteil River (only 10% in 2007). Ammonium flux from the Ponteil River represents 25% in 2007 and 14% in 2008 of the whole ammonium flux that reached the Arcachon lagoon. The Leyre River dominates the DIP flux.

The mean precipitation in 2008 was 984±17 mm. The amount of water supplied by rainfall was compared to the stream flow so that an evaporation rate could be defined. The evaporation rate deduced from the Leyre River daily discharge was around 80%, typical of a forestry catchment (Bosch & Hewlett 1982; Vertessy et al. 2003). The evaporation rate must have been close to 80% in the other studied catchments because the cover is rather similar,

except for some of the highly farmed catchments. The average concentrations of nutrients in rainwater deduced from sample analyses and the precipitations are 0.19 mg N l^{-1} of nitrate, 0.11 mg N l^{-1} of ammonium and 0.004 mg DIP l^{-1}.

Nutrient budget between 1971 and 2008 based on the monitoring of the Leyre River (Auby et al. 1994) shows changes. DIN concentrations and fluxes increased (Fig. 2c,e), whereas DIP concentrations and fluxes decreased (Fig. 2d,f). The interannual nutrient concentration and flux variation was lower than the range of variation between 1970 and 2008. Major changes occurred between 1975 and 1993. During this period, DIN concentrations and fluxes became more than 3 times higher, from 0.33 to 1.2 mg l^{-1} (Fig. 2e), and from 203 to 608 x 10^3 kg-N year^{-1} (Fig. 2c) respectively. This change can be directly related to a change in cultivated surface areas in the catchment. From 1970 to present, the surface area assigned to intensive agriculture has continuously increased in the Leyre catchment according to the data providing by the French agricultural department (Fig. 2a). Simultaneously, the interannual variability has considerably increased. Since 1995, the increase in DIN concentrations and fluxes is lowered despite an increase in cultivated areas. The highest concentration is that reported for the year 2008. The ratio of rainfalls/water discharge increased during the last 15 years (Fig. 2b), suggesting a lowering of Leyre water discharge independent of rainfalls. DIP fluxes dropped from 28 to 4.3 x 10^3 kg year^{-1}. Despite a high variability in concentrations and fluxes, DIP continuously decreased.

Modeling the export rates

The export rates are defined according to the typology based on land-use and summarized in Table 4. Based on the Aiguemorte catchment, forested parcel exports 45 kg N-nitrate km^{-2} year^{-1}. Based on the Cassy catchment the calculated export rate of deforested area is 93 kg N-nitrate km^{-2} year^{-1}. Based on the Betey catchment the export rate of urban area is 62 kg N-nitrate km^{-2} year^{-1}. Based on farmed catchment Leyre, Cires, Milieu, and Passaduy the export rates of cultivated surfaces are 2800, 2900, 2400, and 3300 kg N-nitrate km^{-2} year^{-1}, respectively, i.e. a mean of 2850 kg N-nitrate km^{-2} year^{-1}. The mean export from forested, recently deforested, and farming areas as deduced from catchment slightly impacted by housing is 13 and 0.57 kg km^{-2} year^{-1} for N-ammonium and DIP, respectively. The export rates calculated from the La Teste catchment is indicative of a maximum urban area export.

1   Then, urban areas export 100 kg N-Ammonium km^{-2} $year^{-1}$ and 8.5 kg DIP km^{-2} $year^{-1}$. The

2   DON export is due to the background concentration and equals to 63 kg N km^{-2} $year^{-1}$.

3   The export rates are used to model the annual DIN flux and to validate the model by

4   comparison with data (Tab. 3). The ratio Fm/Fc is close to 1 in the major part of streams for

5   the 2007 year highlighting a good estimate. Two small catchments (Betey, Gujan) are badly

6   modeled because the DIN source due to urban waste is not included in the calculation and the

7   Ponteil catchment is badly modeled too. In 2008, the model is less exact but the main

8   catchment (Leyre) is well modeled with a Fm/Fc ratio equal to 1.2.

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11   *Nitrogen mass balance*

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13   The Figure 3 summarizes the nitrogen mass balance in cultivated pine forests and in

14   cornfields. Inputs are atmospheric deposition, fertilizer, ammonification and nitrification of

15   harvest wastes, and fixation. Outputs are denitrification, volatilization, sorption, harvest, and

16   export by rivers. The two land-use have a different nitrogen mass balance. Fertilizer and

17   harvest are the main nitrogen fluxes in cornfields, whereas atmospheric deposition, fixation

18   and harvest dominate in forest ecosystem.

19   The amount of nitrogen assimilated in mature cornfields is between 22400 and 26400

20   kg N km^{-2} $year^{-1}$ (Plénet & Lemaire 1999). We consider that 60 % is included in grain

21   (Lemaire, comm. pers.) and harvested i.e. 13450 to 15850 kg N km^{-2} $year^{-1}$. Then 40 % stay

22   in situ and are mineralized during the next year i.e. 8950 to 10550 kg N km^{-2} $year^{-1}$. The

23   fixation rate in fields comes from Puckett et al. (1999), but it is not a value from the area

24   studied here. In cornfields of the Arcachon Bay catchment the volatilization rate comes from

25   Jambert et al. (1997), the fertilizer use from Agreste (2000), and the denitrification rate from

26   Rimmelin (1998). In forests, Loustau et al. (1999) estimate the amount of nitrogen assimilated

27   by a 50-years pine forest equals to 50000 kg N including clear-cutting. This nitrogen is

28   contained in trunks (77 %) and in residual parts of trees, mostly barks, or stumps (23 %)

29   (Loustau et al. 1999). As a consequence a 50-years pine forest harvest exports 50000 kg N. At

30   the catchment scale, we consider that this value can be annualized. Then, pine harvesting

31   exports 1000 kg N km^{-2} $year^{-1}$ or 770 kg N km^{-2} $year^{-1}$ if residual parts are not collected. We

32   consider that residual parts may be a source of nitrogen by ammonification, i.e. 220 kg N km^{-2}

33    $year^{-1}$. For maritime pine forests, the N-fixation rate from symbiotic gorse presented in the

Figure 3 comes from Augusto et al. (2005). The estimated annual N_2 fixation flux ranged from 50 to 510 kg N $km^{-1} \cdot year^{-1}$ in the mature pine stands. In young open pine stand, the gorse fixation may reach 5000 kg N $km^{-1} \cdot year^{-1}$. The denitrification rate comes from De Wit et al. (2005), the volatilization rate from Jambert et al. (1994) and the fertilizer use from Loustau et al. (1999) and Blanco (1994). The values are negligible for the balance of nitrogen in forest area.

Discussion

Land use impact on biogeochemistry of the catchments

The nutrient export rate is a function of several environmental parameters including land use (Sobota et al. 2009), hydrology (Obermann et al. 2007) and climate (Howarth et al. 2006). The main variable in the overall studied zone is land use and size of the catchments. Climate, precipitation, and lithology are homogeneous. Relationships between land use and the average nutrient concentration show an obvious positive correlation between the percentage of farming area and the average concentration of nitrate (Fig. 4a). The average nitrate concentration reaches up to 3.5 mg l^{-1} when farming areas occupy more than 20% of the catchment. Thus, nitrate appears as a strong signature of farming areas. Many studies have demonstrated the role of fertilizers in farming areas as a cause of high DIN export in the water system (Galloway 2003; Garcia-Esteves et al. 2007). DON concentrations are lower than DIN concentrations and do not correlate with farming area highlighting that fields of the Arcachon catchment export more nutrients as inorganic species. The dominance of DIN versus DON is classically observed for south European regions (Lorite-Herrera et al. 2009) whereas north European fields preferentially export nutrients as organic species (Agedah et al. 2009; Stedmon et al. 2006).

Average ammonium and DIP concentrations are correlated with the percentage of housing areas, with correlation coefficient equal to 0.836 and 0.734 respectively (Fig. 4b,c). The correlation between ammonium concentration and housing area excludes the Ponteil

catchment, which seems to have an atypical behavior (Canton et al. 2010). Wastewaters of the cities around the Arcachon Bay are collected, treated and flushed out the lagoon. We have observed, however, a slight effect of housing on the quality of streamwaters. It may partially be due to urban runoff. Nevertheless, DIP concentrations are very low in comparison with major French rivers, with 0.025 to 0.047 mg l^{-1} reported in the Garonne River (Deborde et al. 2007; Muylaert et al. 2009) and 0.062 mg l^{-1} reported for the Loire River (Moatar & Meybeck 2005). Due to a large amount of iron oxides and humic particles the Landes de Gascogne soils are favorable to DIP sorption (Qualls et al. 2002). Hence, the DIP export is highly limited. Wastewaters of the municipalities located upstream of the Leyre River are treated and flushed into the river. Moreover, the wastewater collect of the small littoral catchments is more efficient than those of the Leyre catchment. This may explain the relatively high concentrations of DIP in the Leyre River versus the small littoral catchments. Consequently, DIP and ammonium originate mostly from point sources related to urban area, but the wastewater discharge in the river system is highly changeable.

Pine forests are known to export fewer nutrients than grassland or fields (Benoit et al. 1995; Onderka et al. 2009), by limiting runoff and leakage of nutrients. The cultivated pine forest of the studied area does not receive fertilizers, except a phosphorus fertilization before plantation (Blanco 1994). DON represents up to 65% of the total nitrogen export in strictly non-farmed catchments. This ratio between DON and DIN is frequently observed in forest ecosystems (Hedin & Johnson 1995; Perakis & Hedin 2002) except in highly anthropized forests (Campbell et al. 2000). Dominance of DON export is explained by an efficient denitrification and uptake in riparian zone, which decreases the DIN export (Vink et al. 2007) and because riparian zone is a source of DON from root exudation (Hagedorn et al. 2001). In the Arcachon Bay catchment, DON concentration does not characterize forested surfaces, because we have observed no correlation between these two parameters (Fig. 4d). The main part of the studied catchments contain between 70 and 80 % of forested area but DON concentrations are between 0.07 and 0.63 mg l^{-1} and the most often between 0.21 and 0.35 mg l^{-1}. Then DON should be rather a background concentration of all soil type leaching.

Updating the eutrophication risk of the Arcachon Bay

A moderate eutrophication was observed in the Arcachon lagoon during the eighties in late spring and summer (Auby et al. 1994). The most significant change among primary producers was the development of the allochtonous green algae *Monostroma obscurum*. The biomass of this macro algae reached 18 000 to 21 000 x 10^3 kg in spring during the eighties and the nineties (Auby et al. 1994). The proliferation was due to eutrophication of the lagoon and the invasive development of the algae. Moreover, *Monostroma obscurum* is highly competitive, particularly in P-limiting conditions, and can store nutrients to build resistance during the oligotrophic period (Auby et al. 1994). The European projects CLEAN (Coastal Lagoon Eutrophication and Anaerobic Processes, 1996) and ROBUST (the ROle of BUffering capacities in STabilising coastal lagoon ecosystems, 1996-1999) have contributed toward characterizing the origin and effect of eutrophication in the Bay (Castel et al. 1996; De Wit et al. 2001): the increase in nutrient discharge originating from continent was the major cause of eutrophication. This eutrophication was partially buffered by *Zostera noltii* meadows and Arcachon Bay sediments, the both acting as sink of nutrient. In addition to the nutrient concentration, the low residual currents favoured eutrophication. The average residence time of water ranges from 12.5 to 15.9 days in the Arcachon Bay (Plus et al. 2009). It contrasts, for example, with the bay of Brest, also located in the French Atlantic coast, which is well resistant to eutrophication as the hydrodynamics allows quick dispersion of living matter and nutrients (Le Pape et al. 1996), despite very high inputs of continental DIN. The residence time of fresh waters makes the Arcachon Bay very sensitive to the change of nutrient fluxes with time. Presently, blooms of macro algae are no longer reported and the primary production is now dominated by the microphytobenthos and phytoplankton (Glé et al. 2007), and the natural meadows of *Zostera noltii* (Auby 1991) although, the DIN flux has not decreased since the eighties (Fig. 2c). However, the DIP flux has decreased (Fig 2d). It suggests that the past high fluxes of DIP were responsible for the summer blooms. Another point of view is to consider a biological feedback due to the macro algae proliferation, regardless of nutrient input. After a rapid proliferation for years, the introduced species may have found a biological steady state including a regulation due to predation.

Since 1995 the DIN flux has been more or less stable. This is not due to the stabilization of the agricultural surface area. This surface area has continuously increased since 1970 (Fig 2a), which probably explains a continuously increase in DIN concentrations (Fig. 2e). The fact is that the Leyre River water discharge has slightly decreased (Fig. 2b), which may be the reason for the relative stabilization in DIN fluxes. The ratio of rainfalls/water discharge increased during the last 15 years (Fig. 2b), suggesting a lowering of

1   Leyre water discharge, independent of rainfalls. This low water discharge may be due to

2   cornfield irrigation. DIN fluxes stabilization might be also the consequence of a better control

3   in fertilizer use. The decrease in DIP fluxes and concentrations must be the consequence of

4   wastewater management improvement during these decades. As a consequence the

5   eutrophication risk is probably as high as that during the eighties. The recent regression of

6   *Zostera noltii* meadows (Plus et al. 2010), however, may increase the eutrophication risk

7   because these meadows buffer the nutrient loads (De Wit et al. 2001).

8   The quality of atmospheric deposition is more or less constant. The DIN flux in 2008

9   was 287 kg N- km^{-2} year^{-1}. This represents half the value of the atmospheric DIN flux

10   reported by Auby et al. (1994) but the same order of that reported by Collos et al. (1989).

11   Despite the high variability, these values are between pristine sites, (Owens et al. 1992) and

12   coastal and anthropized areas (Cornell et al. 1995). The Arcachon lagoon comes under the

13   category of preserved sites but not pristine. Consequently, atmospheric depositions are not a

14   cause of eutrophication of the lagoon at the present time.

15

16

17   *Nitrogen mass balance validation and assessment of the*

18   *durability of maize and pine crop*

19

20   The export rates are calculated from one year of samplings in rivers and analyses. As a

21   consequence, they describe the nutrient export during a short time and may not be applicable

22   for every year. The nitrate export rate due to forest parcel (45 kg N-nitrate km^{-2} year^{-1}) is

23   comparable to the value of 38 kg N-nitrate km^{-2} year^{-1} reported for the Tagon catchment (De

24   Wit et al. 2005). In 2007-2008, the export rate of the Tagon catchment reached 88 kg N-

25   nitrate km^{-2} year^{-1}, suggesting that an additional source of nitrate was present in this

26   catchment, probably linked to deforested parcels. Our result suggests that tree harvesting

27   increases the nitrate export (93 kg N-nitrate km^{-2} year^{-1}), as reported for alpine forests

28   (Bäumler & Zech 1999) and temperate forests (Likens et al. 1970). For instance, the export

29   rate reported for the Hubbard Brook forest was 142 kg N-nitrate km^{-2} year^{-1} within two years

30   following the deforestation (Likens et al. 1970). The export rates of cultivated surfaces are

31   2800, 2900, 2400, and 3300 kg N-nitrate km^{-2} year^{-1} in Leyre, Cires, Milieu, and Passaduy

32   catchments, respectively i.e. a mean of 2850 kg N-nitrate km^{-2} year^{-1}. Differences between

1   catchments may be due to the kind and history of farming. Indeed, cornfields dominates the

2   farming areas, but vegetable and flowers fields occupy about 30% of farming surfaces. The

3   DIN export rate certainly depends on this land-use parameter. The size of the watershed

4   should probably also be taken into account. The Leyre catchment is larger than the other

5   catchments: cornfields are located far from the sampling station. As a consequence the Leyre

6   river may loss a part of nitrate by plant uptake or denitrification along the riverbed.

7   The modeled nitrate flux is in very good agreement with the measured nitrate flux for

8   the Leyre River in 2007 and good in 2008 (Tab. 3). The differences between modeled and

9   measured fluxes are higher for Cires and Milieu catchments. Several authors have

10 demonstrated that nutrient fluxes increases with river discharge due to intensification of

11 runoff and leaching (Dumont et al. 2005; Holloway & Dahlgren 2001; Obermann et al. 2007;

12 Probst 1985; Schaefer et al. 2009). The calculated nitrate export rate does not include the

13 variations of stream water discharge. It may explain the difference between 2007 and 2008

14 particularly in small catchments, because they are more reactive to flood events. The well

15 modeled Leyre River represents 90 % of the total DIN flux toward the Arcachon Bay.

16 Therefore the nitrate export rate due to farming parcels is a good approximation for this first

17 nitrogen mass balance.

18   The mineralization rate may be overestimated because we consider that the total

19 biomass of maize stems and leaves is mineralized. However nitrogen may be lost in refractory

20 organic matter or by grazing. The denitrification rate under cornfields may be overestimated

21 too. Although a high potential of denitrification was measured (Rimmelin 1998) the low

22 amount of organic carbon in soils is highly limiting (De Wit et al. 2005).

23   Since the different sinks and sources of nitrogen are estimated with large error

24 margins, we discuss several budgets. In cornfields, the maximum nitrogen input is about

25 31400 kg DIN km^{-2} $year^{-1}$ and the minimum is equal to 27800 kg DIN km^{-2} $year^{-1}$. The

26 maximum nitrogen output is equal to about 27600 kg DIN km^{-2} $year^{-1}$ and the minimum is

27 equal to 25000 kg DIN km^{-2} $year^{-1}$. Considering these results cornfields gain nitrogen. The

28 benefit is between 200 and 6400 kg DIN km^{-2} $year^{-1}$. The excess of DIN input may be

29 compensated by storage as organic nitrogen forms. This organic nitrogen is not exported by

30 rivers, as demonstrated above, and may be stored in soil. Howarth et al. (2006) have observed

31 nitrogen storage in soils, which occurred preferentially during dry years; nitrogen was flushed

32 during wet years. Moreover, we assume that the mineralization rate of leaves and stems of

33 maize is overestimated because a part may be stored. Fixation should be overestimated too

34 because we do not have data from the studied area. Since fertilizer is the main source of DIN

and nitrogen is in excess, the fertilizer use should be reduced. DIN export by river represents between 4.8 and 5.4 % of the total nitrogen cycle in cornfields and between 3.3 and 4.2 % in pine forest. It suggests that cornfields are more impacted by DIN leaching and run-off.

We identify only two sinks of nitrogen in mature pine forest: harvest and river export. Forest harvesting is the major sink of nitrogen but it depends of the fate of barks. If barks are harvested then nitrogen output is equal to about 1060 kg DIN km^{-2} $year^{-1}$ and nitrogen input is between 350 and 810 kg DIN km^{-2} $year^{-1}$. If barks are not harvested then nitrogen output is equal to 830 kg DIN km^{-2} $year^{-1}$ and nitrogen input is between 570 and 1030 kg DIN km^{-2} $year^{-1}$. The DIN budget in forest is highly variable because of the wide interval of values for N-fixation rates. Nitrogen outputs are generally higher than inputs. Consequently the cultivated pine forest is not sustainable. However, the N_2-fixation rate may be underestimated and in-situ measurements are needed in order to validate this mass balance.

Conclusion

A detailed study of small catchments enables a mechanistic approach of nutrient dynamics in relation to land use. Such an approach has already been followed in the area considered in this study for the Ponteil and the Tagon Rivers (Canton et al. 2010; De Wit et al. 2005). Data on nutrient fluxes as well as land use analysis of all the catchments allowed us to provide an estimate of continental dissolved N and P fluxes to the Arcachon Bay and to connect export by rivers to land use.

We emphasize a net impact of land-use on stream water quality. Agriculture is the major source of nitrogen for the lagoon and it has a robust signature on stream water. Farming parcels export 2863 kg DIN km^{-2} $year^{-1}$ including 99.5 % of nitrate. This average rate permits a good prevision of the DIN flux in the larger catchment (Leyre River) but it is less accurate in smaller catchment due to high interannual variability. It permits to obtain, however, a good assessment of the nitrate flux entering in the lagoon, since the Leyre River represents a total of 90 % of the continental DIN flux. The nitrate flux modeling can be improved by the integration of stream water discharge especially in small catchment. We have estimated the nitrate export rate originating from forest parcels and deforested parcels to 45 and 93 kg N

km^{-2} year^{-1}, respectively. The ammonium and DIP export rates are independent of land-use and equal to 13 kg N km^{-2} year^{-1} and 0.57 kg P km^{-2} year^{-1} respectively. Nutrient export by urban area is highly variable depending of the quality of wastewater treatment. DON has a background concentration independent of land-use.

This study completes and unifies several studies. (i) First, it permits to have a long-term view of land-use and nutrient budget change. The nitrogen flux has increased between 1970 and 1995 and it is more or less constant since 1995 because of the decrease in stream water discharge. Thus the increase in irrigation due to maize cultivation limits nitrogen exportation. Of course, this should probably have an unknown impact on the budget of the freshwater in the Arcachon lagoon. The DIP flux has decreased continuously since 1970 due to wastewater treatment improvement. As a consequence the risk of eutrophication of the Arcachon Bay is now reduced in comparison with the eighties. (ii) Secondly, this study permits to establish and compare the nitrogen budget in cornfields and cultivated pine forest. We highlight that the nitrogen management is not optimal in cornfields and the soils store between 200 and 6400 kg DIN km^{-2} year^{-1}. Therefore, the fertilizer use should be reduced. The nitrogen budget in cultivated forest emphasizes that the soils may lose nitrogen when harvesting is done every 50 years and if the fixation rate is minimum. However, the nitrogen mass balance highlights a lack of data on nitrogen fixation rate in the two studied ecosystems.

1 **Figure captions**

2

3 Figure 1: General view and soil occupation in the Arcachon Bay catchment. Soil occupation

4 is determined by analyzing plane photography in Geographic Information System (GIS).

5 Catchment boundaries are defined in Laplana (1992).

6

7 Figure 2: Change in nutrient export by the Leyre River and catchment characteristics between

8 1970 and 2008. (a) shows the change in farming surface area in km^2; (b) shows the change of

9 rainfalls/water discharge ratio; (c) shows the change of DIN flux in 10^3 $kg\text{-}N.year^{-1}$; (d) shows

10 the change of DIP flux in 10^3 $kg\text{-}P.year^{-1}$; (e) shows the change of DIN concentration in

11 $\mu mol.L^{-1}$; (f) shows the change of DIP concentration in $\mu mol.L^{-1}$. White diamonds are data

12 originating from Auby (1991), Laplana (1992), and Ifremer surveys, and black squares are

13 from the present study

14

15 Figure 3: Comparison of nitrogen mass balance in two agro ecosystems, cornfield and

16 cultivated pine forest. The dark grey symbolizes nitrogen output and the slight grey

17 symbolizes nitrogen input.

18

19 Figure 4: Typology based on land use and nutrient concentrations. (a) shows the relation

20 between average nitrate concentrations by catchment and farming area; (b) shows the relation

21 between average ammonium concentrations by catchment and housing area; (c) shows the

22 relation between average dissolved inorganic phosphorus concentrations by catchment and

23 farming area; and (d) shows the relation between average dissolved organic nitrogen

24 concentrations by catchment and forest area.

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Agedah EC, Binalaiyifa HE, Ball AS, Nedwell DB (2009) Sources, turnover and bioavailibility of dissolved organic nitrogen in the Colne estuary, UK. Marine Ecology Progress Series 382: 23-33

AGRESTE (2000) Recensements agricoles. In. Ministère de l'Agriculture.

Anderson L (1979) Simultaneous spectrophotometric determination of nitrite and nitrate by flow injection analysis. Analytica Chimica Acta 110: 123-128

Auby I (1991) Contribution à l'étude des herbiers de Zostera noltii dans le Bassin d'Arcachon : dynamique, production et dégradation, macrofaune associée. In. University of Bordeaux. p 234

Auby I, Labourg PJ (1996) Seasonal dynamics of Zostera noltii Hornem. In the Bay of Arcachon (France). Journal of Sea Research 35(4): 269-277

Auby I, Manaud F, Maurer D, Trut G (1994) Etude de la prolifération des algues vertes dans le bassin d'Arcachon. Report Prepared by IFREMER, Arcachon, France, for CEMAGREF-SSA-SABARC: 1-163

Augusto L, Crampon N, Saur E, Bakker MR, Pellerin S, De Lavaissière C, Trichet P (2005) High rates of nitrogen fixation of Ulex species in the understory of maritime pine stands and the potential effect of phosphorus fertilization. Canadian Journal of Forest Research 35(5): 1183-1192

Bäumler R, Zech W (1999) Effects of forest thinning on the streamwater chemistry of two forest watersheds in the Bavarian Alps. Forest Ecology and Management 116(1-3): 119-128

Benoit M, Saintot D, Gaury F (1995) Mesures en parcelles d'agriculteurs des pertes en nitrates. Variabilité sous divers systèmes de culture et modélisation de la qualité de l'eau d'un bassin d'alimentation. In: C.R. Acad. Agr. p 175-188

Billen G, Garnier J, Némery J, Sebilo M, Sferratore A, Barles S, Benoit P, Benoît M (2007) A long-term view of nutrient transfers through the Seine river continuum. Science of the Total Environment 375(1-3): 80-97

Blanco C (1994) Le pin maritime, son environnement, sa culture, les facteurs climatiques et fongiques responsables de son affaiblissement. In. University Bordeaux 2, Bordeaux. p 68

Bosch JM, Hewlett JD (1982) A review of catchment experiments to determine the effect of vegetation changes on water yield and evapotranspiration. Journal of Hydrology 55(1-4): 3-23

Campbell JL, Hornbeck JW, McDowell WH, Buso DC, Shanley JB, Likens GE (2000) Dissolved organic nitrogen budgets for upland, forested ecosystems in New England. Biogeochemistry 49(2): 123-142

Canton M, Anschutz P, Naudet V, Molnar N, Mouret A, Franceschi M, Naessens F, Poirier D (2010) Impact of solid waste disposal on nutrient dynamics in a sandy catchment. Journal of Contaminant Hydrology 116(1-4): 1-15

Castel J, Caumette P, Herbert R (1996) Eutrophication gradients in coastal lagoons as exemplified by the Bassin d'Arcachon and the Etang du Prévost. Hydrobiologia 329(1-3):

Collos Y, Souchu P, Tréguer P (1989) Relationships between different forms of inorganic nitrogen in rainwater of a coastal area and ground-level gaseous nitrogen oxides. Atmospheric Research 23(2): 97-104

Conley DJ, Schelske CL, Stoermer EF (1993) Modification of the biogeochemical cycle of silica with eutrophication. Marine Ecology Progress Series 101(1-2): 179-192

Cornell S, Rendell A, Jickells T (1995) Atmospheric inputs of dissolved organic nitrogen to the oceans. Nature 376(6537): 243-246

De Wit R, Leibreich J, Vernier F, Delmas F, Beuffe H, Maison P, Chossat JC, Laplace-Treyture C, Laplana R, Clave V, Torre M, Auby I, Trut G, Maurer D, Capdeville P (2005) Relationship between land-use in the agro-forestry system of les Landes, nitrogen loading to and risk of macro-algal blooming in the Bassin d'Arcachon coastal lagoon (SW France). Estuarine, Coastal and Shelf Science 62(3 SPEC. ISS.): 453-465

De Wit R, Stal LJ, Lomstein BA, Herbert RA, Van Gemerden H, Viaroli P, Cecherelli VU, Rodriguez-Valera F, Bartoli M, Giordani G, Azzoni R, Schaub B, Welsh DT, Donnelly A, Cifuentes A, Anton J, Finster K, Nielsen LB, Pedersen AGU, Neubauer AT, Colangelo MA, Heijs SK (2001) Robust: The role of buffering capacities in stabilising coastal lagoon ecosystems. Continental Shelf Research 21(18-19): 2021-2041

Deborde J, Anschutz P, Chaillou G, Etcheber H, Commarieu MV, Lecroart P, Abril G (2007) The dynamics of phosphorus in turbid estuarine systems: Example of the Gironde estuary (France). Limnology and Oceanography 52(2): 862-872

Diaz RJ, Rosenberg R (2008) Spreading dead zones and consequences for marine ecosystems. Science 321(5891): 926-929

Duarte CM (1995) Submerged aquatic vegetation in relation to different nutrient regimes Ophelia 41: 87-112

Dumont E, Harrison JA, Kroeze C, Bakker EJ, Seitzinger SP (2005) Global distribution and sources of dissolved inorganic nitrogen export to the coastal zone: Results from a spatially explicit, global model. Global Biogeochemical Cycles 19(4):

Falkowski PG, Barber RT, Smetacek V (1998) Biogeochemical controls and feedbacks on ocean primary production. Science 281(5374): 200-206

Galloway JN (1998) The global nitrogen cycle: changes and consequences. Environmental Pollution 102(1, Supplement 1): 15-24

Galloway JN (2003) The Global Nitrogen Cycle. In: Elsevier (ed) Treatise on Geochemistry. p 557-583

Garcia-Esteves J, Ludwig W, Kerhervé P, Probst J-L, Lespinas F (2007) Predicting the impact of land use on the major element and nutrient fluxes in coastal Mediterranean rivers: The case of the Têt River. Applied Geochemistry 22(1): 230-248

Glé C, Del Amo Y, Sautour B, Laborde P, Chardy P (2007) Variability of nutrients and phytoplankton primary production in a shallow macrotidal coastal ecosystem (Arcachon Bay, France). Estuarine, Coastal and Shelf Science 76(3): 642-656

Groffman PM, Tiedje JM (1989) Denitrification in north temperate forest soils: Relationships between denitrification and environmental factors at the landscape scale. Soil Biology and Biochemistry 21(5): 621-626

Hagedorn F, Bucher JB, Schleppi P (2001) Contrasting dynamics of dissolved inorganic and organic nitrogen in soil and surface waters of forested catchments with Gleysols. Geoderma 100(1-2): 173-192

Hedin AJ, Johnson A (1995) Patterns of nutrient loss from unpolluted, oldgrowth temperate forests: evaluation of biogeochemical theory. Ecology 76: 493-509

Holloway JM, Dahlgren RA (2001) Seasonnal and event-scale variations in solute chemistry for four Sierra Nevada catchments. Journal of Hydrology 206: 106-121

Howarth RW (2008) Coastal nitrogen pollution: A review of sources and trends globally and regionally. Harmful Algae 8(1): 14-20

Howarth RW, Marino R (2006) Nitrogen as the limiting nutrient for eutrophication in coastal marine ecosystems: Evolving views over three decades. Limnology and Oceanography 51(1 II): 364-376

Howarth RW, Swaney DP, Boyer EW, Marino R, Jaworski N, Goodale C (2006) The influence of climate on average nitrogen export from large watersheds in the Northeastern United States. Biogeochemistry 79(1-2): 163-186

Jambert C, Delmas RA, Labroue L, Chassin P (1994) Nitrogen compound emissions from fertilized soils in a maize field pine tree forest agrosystem in the southwest of France. Journal of Geophysical Research 99(D8):

Jambert C, Serça D, Delmas R (1997) Quantification of N-losses as NH3, NO, and N2O and N2 from fertilized maize fields in southwestern France. Nutrient Cycling in Agroecosystems 48(1-2): 91-104

Laplana R, Billy F, Beuffe H, Fleuranceau F (1992) Localisation, quantification et dynamique des apports de nutriments au Bassin d'Arcachon. Localisation, Quantification et Dynamique des Apports de Nutriments au Bassin d'Arcachon 66:

Le Pape O, Del Amo Y, Menesguen A, Aminot A, Quequiner B, Treguer P (1996) Resistance of a coastal ecosystem to increasing eutrophic conditions: The Bay of Brest (France), a semi-enclosed zone of Western Europe. Continental Shelf Research 16(15): 1885-1907

Legigan P (1979) L'élaboration de la formation du Sable des Landes, dépot résiduel de l'environnement sédimentaire pliocène-pléistocène centre aquitain. In. Université de Bordeaux, Bordeaux. p 429

Likens EG, Bormann FH, Johnson MN, Fisher DW, Pierce SR (1970) Effects of Forest Cutting and Herbicide Treatment on Nutrient Budgets in the Hubbard Brook Watershed-Ecosystem. Ecological Monographs 40(1): 23-47

Lorite-Herrera M, Hiscok K, Jiménez-Espinosa R (2009) Distribution of Dissolved Inorganic and Organic Nitrogen in river water and groundwater in an agriculturally-dominated catchment, south-east Spain. Water Air Soil Pollution 2009(198): 335-346

Loustau D, Bert D, Trichet P (1999) Fonctionnement primaire et productivité de la forêt landaise : implication pour une gestion durable. Revue Forestière Française 51(5): 571-592

Ludwig W, Probst JL (1998) River sediment discharge to the oceans; present-day controls and global budgets. American Journal of Science 298: 265-295

Mantoura RFC, Martin JM, Wollast R (1991) Ocean margin processes in global change. Report of the Dahlem workshop, Berlin, March 1990.

Meybeck M, Helmer R (1989) The quality of rivers: From pristine stage to global pollution. Global and Planetary Change 1(4): 283-309

Meybeck M, Ragu A Presenting the GEMS-GLORI, a compendium of world river discharge to the oceans. In: Freshwater Contamination. Rabat. 1997. vol 243. p 3-14

Moatar F, Meybeck M (2005) Compared performances of different algorithms for estimating annual nutrient loads discharged by the eutrophic River Loire. Hydrological Processes 19(2): 429-444

Mullin JB, Riley JP (1955) The colorimetric determination of silicate with special reference to sea and natural waters. Analytica Chimica Acta 12: 162-176

Murphy J, Riley JP (1962) A modified single solution method for the determination of phosphate in natural waters. Analytica Chimica Acta 27: 31-36

Muylaert K, Sanchez-Pérez JM, Teissier S, Sauvage S, Dauta A, Vervier P (2009) Eutrophication and its effect on dissolved Si concentrations in the Garonne River (France). Journal of Limnology 68(2): 368-374

Nixon SW, Buckley B, Granger S, Bintz J (2001) Responses of very shallow marine ecosystems to nutrient enrichment. Human & Ecological Risk Assessment 7: 1457-1481

Obermann M, Froebrich J, Perrin JL, Tournoud MG (2007) Impact of significant floods on the annual load in an agricultural catchment in the mediterranean. Journal of Hydrology 334(1-2): 99-108

Onderka M, Pekarova P, Miklanek P, Halmova D, Pekar J (2009) Examination of the Dissolved Inorganic Nitrogen Budget in Three Experimental Microbasins with Contrasting Land Cover- A Mass Balance Approach. Water, Air, and Soil Pollution: 1-10

Owens NJP, Galloway JN, Duce RA (1992) Episodic atmospheric nitrogen deposition to oligotrophic oceans. Nature 357(6377): 397-399

Perakis S, Hedin AJ (2002) Fluxes and fates of nitrogen in soil of an unpolluted old-growth temperate forest, southern Chile. Ecology 82: 2245-2260

Plénet D, Lemaire G (1999) Relationships between dynamics of nitrogen uptake and dry matter accumulation in maize crops. Determination of critical N concentration. Plant and Soil 216(1-2): 65-82

Plus M, Dalloyau S, Trut G, Auby I, de Montaudouin X, Emery E, Noël C, Viala C (2010) Long-term evolution (1988-2008) of Zostera spp. meadows in Arcachon Bay (Bay of Biscay). Estuarine, Coastal and Shelf Science 87: 357-366

Plus M, Dumas F, Stanisière JY, Maurer D (2009) Hydrodynamic characterization of the Arcachon Bay, using model-derived descriptors. Continental Shelf Research 29(8): 1008-1013

Probst JL (1985) Nitrogen and Phosphorus exportation in the Garonne Basin (France). Journal of Hydrology 76(3-4): 281-305

Puckett LJ, Cowdery TK, Lorenz DL, Stoner JD (1999) Estimation of nitrate contamination of an agro ecosystem outwash aquifer using a nitrogen mass balance budget. Journal of Environmental Quality 28: 2015-2025

Qualls RG, Haines BL, Swank WT, Tyler SW (2002) Retention of soluble organic nutrients by a forested ecosystem. Biogeochemistry 61(2): 135-171

Rimmelin P (1998) Etude des apports allochtones d'azote inorganique dissous parvenant à un système lagunaire : le Bassin d'Arcachon. In. University Bordeaux 1, Bordeaux.

Rimmelin P, Dumon JC, Maneux E, GonCalves A (1998) Study of Annual and Seasonal Dissolved Inorganic Nitrogen Inputs into the Arcachon Lagoon, Atlantic Coast (France). Estuarine, Coastal and Shelf Science 47(5): 649-659

Saint Pe MA (1966) Etude Hydrogéologique et Géochimique: la Nappe Phréatique du Nord-est du Bassin d'Arcachon et son Influence sur l'Alimentation des Aquifères Sous-Jacents. In. Université de Bordeaux. p 439

1 Schaefer SC, Hollibaugh JT, Alber M (2009) Watershed nitrogen input and riverine export on the
2   west coast of the US. Biogeochemistry 93(3): 219-233

3 Smith VH (2003) Eutrophication of freshwater and coastal marine ecosystems: A global problem.
4   Environmental Science and Pollution Research 10(2): 126-139

5 Sobota DJ, Harrison JA, Dahlgren RA (2009) Influences of climate, hydrology, and land use on
6   input and export of nitrogen in California watersheds. Biogeochemistry 94(1): 1-20

7 Stedmon CA, Markaker S, Søndergaard M, Vang T, Laubel A, Borch NH (2006) Dissolved
8   organic matter export to a temperate estuary; seasonal variations and implications of land-use.
9   Estuarine, Coastal and Shelf Science 29: 388-400

10 Strickland JDH, Parsons TR (1972) A pratical handbook of seawater analysis. Bulletin of
11   Fisheries Research Board of Canada:

12 Valderrama JC (1981) The simultaneous analysis of total nitrogen and total phosphorus in natural
13   waters. Marine Chemistry 10(2): 109-122

14 Valiela I, McClelland J, Hauxwell J, Behr PJ, Hersh D, Foreman K (1998) Macroalgal blooms in
15   shallow estuaries: Controls and ecophysiological and ecosystem consequences. Limnology
16   and Oceanography 42(5 II): 1105-1118

17 Vertessy RA, Zhang L, Dawes WR (2003) Plantations, river flows and river salinity. Australian
18   Forestry 66(1): 55-61

19 Vink S, Ford PW, Bormans M, Kelly C, Turley C (2007) Contrasting nutrient exports from a
20   forested and an agricultural catchment in south-eastern Australia. Biogeochemistry 84(3):
21   247-264

22 Walling DE, Webb BW (1985) Estimating the discharge of contaminants to coastal waters by
23   rivers: some cautionary comments. Marine Pollution Bulletin 16(12): 488-492

24
25
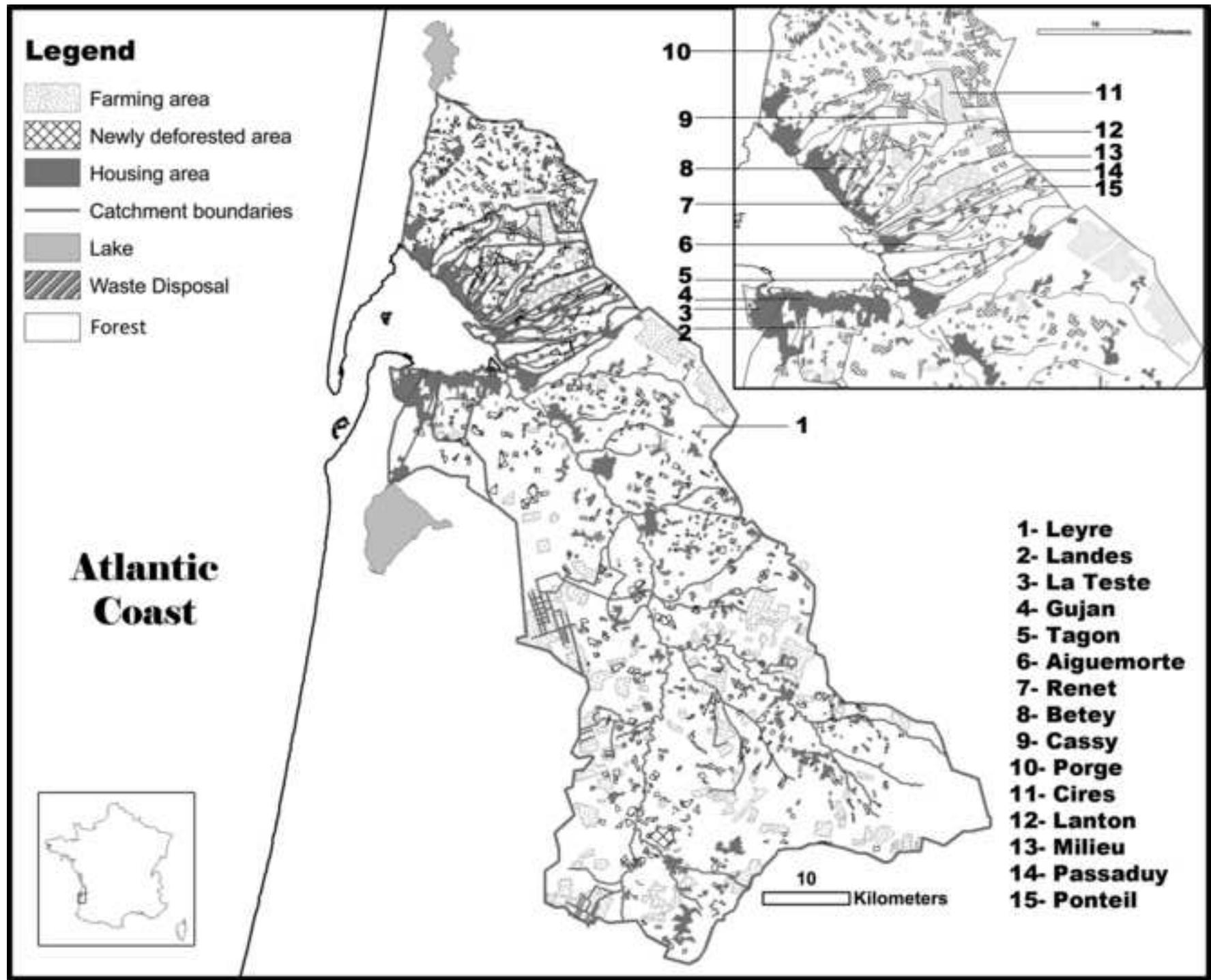
Figure 1
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Figure 1
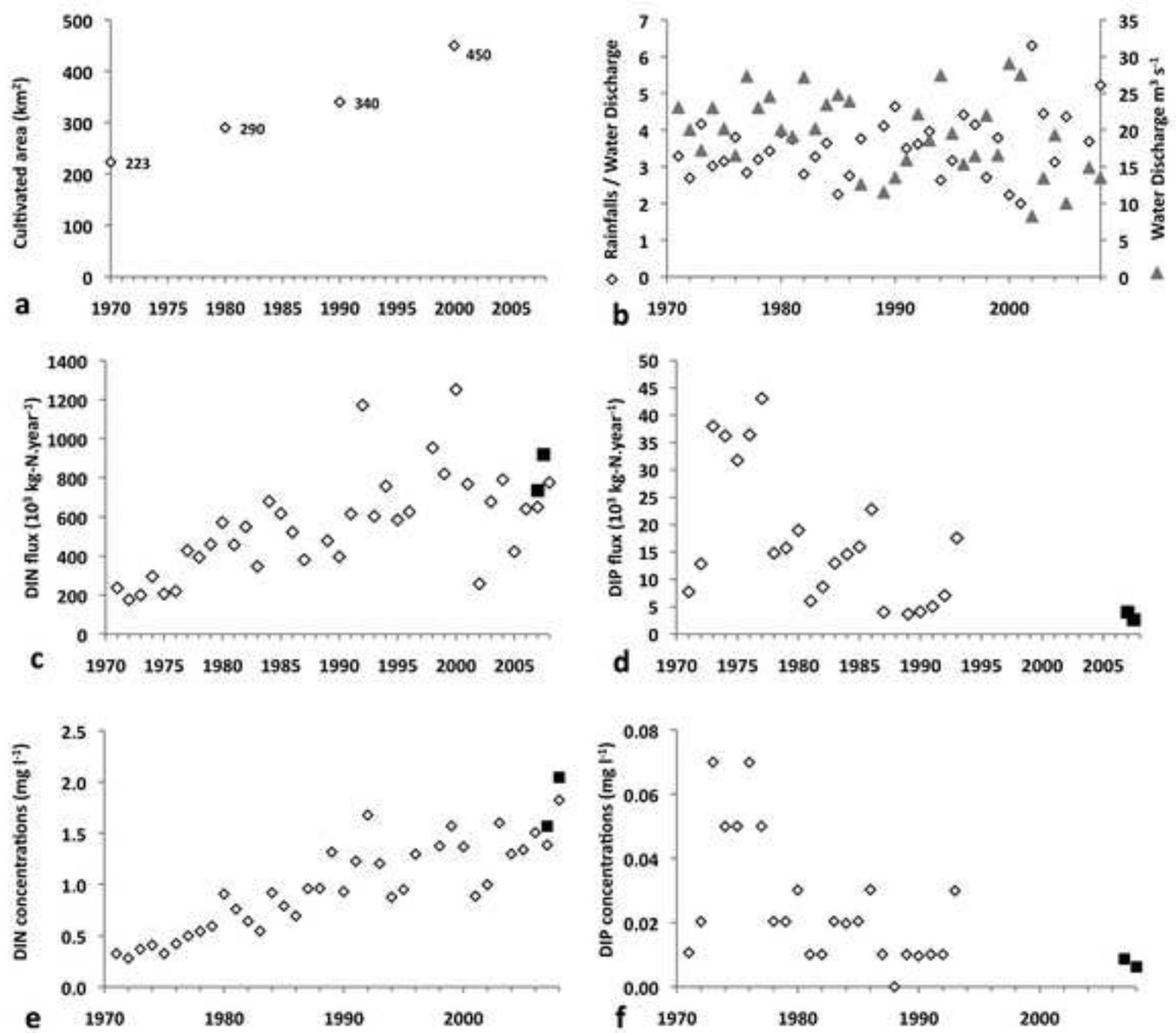
Figure 3

Nitrogen mass balance in cornfields
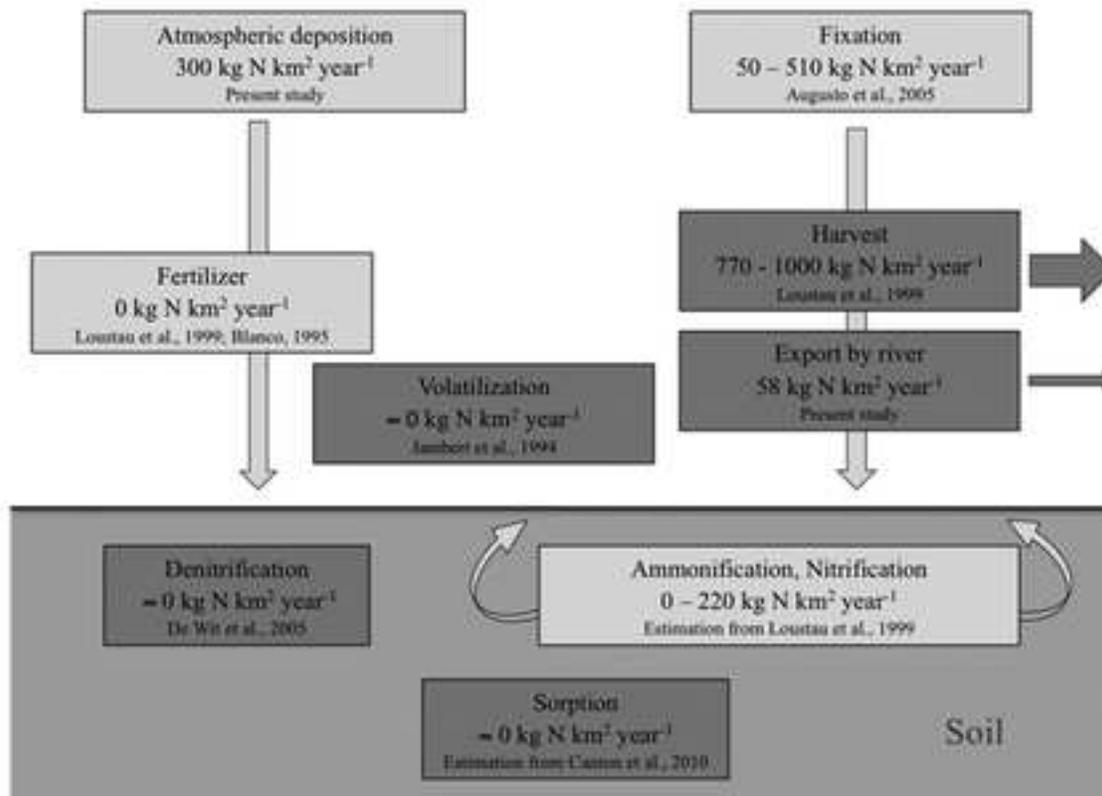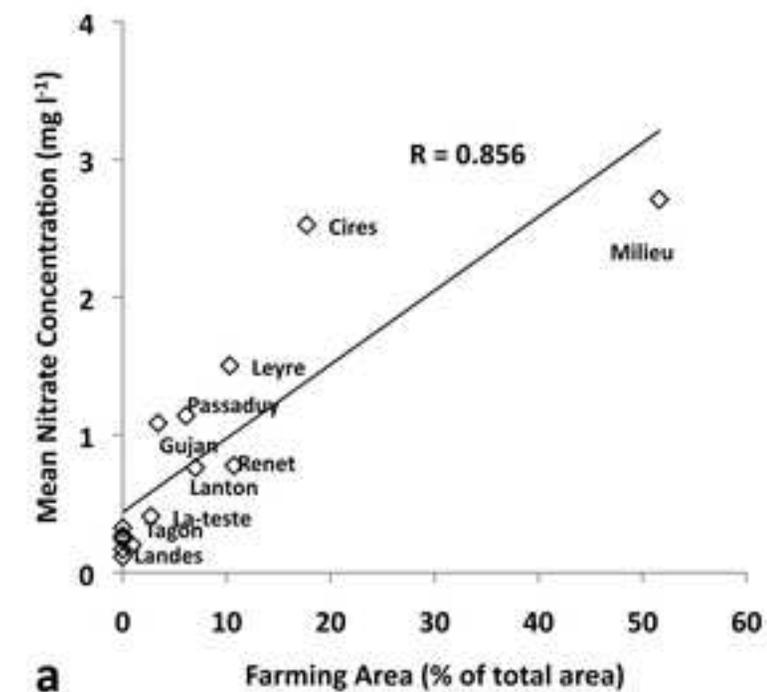
Atmospheric deposition
300 kg N km² year⁻¹
Present study

Fixation
500 – 1500 kg N km² year⁻¹
Puckett et al., 1999

Fertilizer
18000 – 19000 kg N km² year⁻¹
Agreste, 2000

Harvest
13450 – 15850 kg N km² year⁻¹
Estimation from Agreste, 2000; Plénet and Lemaire, 1999

Volatilization
110 – 275 kg N km² year⁻¹
Jambert et al., 1997

Export by river
2863 kg N km² year⁻¹
Present study

Denitrification
8600 kg N km² year⁻¹
Rimmelin, 1998

Ammonification, Nitrification
8950 – 10550 kg N km² year⁻¹
Estimation from Plénet and Lemaire, 1999; Bricas et al., 1995

Sorption
≈ 0 kg N km² year⁻¹
Estimation from Canton et al., 2010

Soil

Nitrogen mass balance in pine forest

Atmospheric deposition
300 kg N km² year⁻¹
Present study

Fixation
50 – 510 kg N km² year⁻¹
Augusto et al., 2005

Fertilizer
0 kg N km² year⁻¹
Loustau et al., 1999; Blanco, 1995

Harvest
770 - 1000 kg N km² year⁻¹
Loustau et al., 1999

Volatilization
≈ 0 kg N km² year⁻¹
Jambert et al., 1998

Export by river
58 kg N km² year⁻¹
Present study

Denitrification
≈ 0 kg N km² year⁻¹
De Wit et al., 2005

Ammonification, Nitrification
0 – 220 kg N km² year⁻¹
Estimation from Loustau et al., 1999

Sorption
≈ 0 kg N km² year⁻¹
Estimation from Canton et al., 2010

Soil

Figure 4
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a — Mean Nitrate Concentration (mg l⁻¹) vs Farming Area (% of total area), R = 0.856

b — Mean Ammonium Concentration (mg l⁻¹) vs Housing Area (% of total area), R = 0.836

c — Mean DIP Concentration (mg l⁻¹) vs Housing Area (% of total area), R = 0.784

d — Mean DON Concentration (mg l⁻¹) vs Forested Area (% of total area)
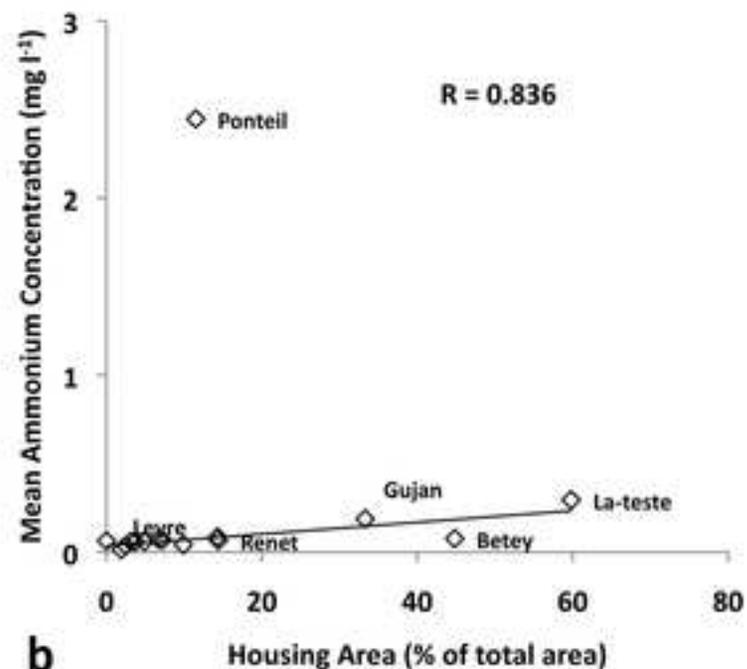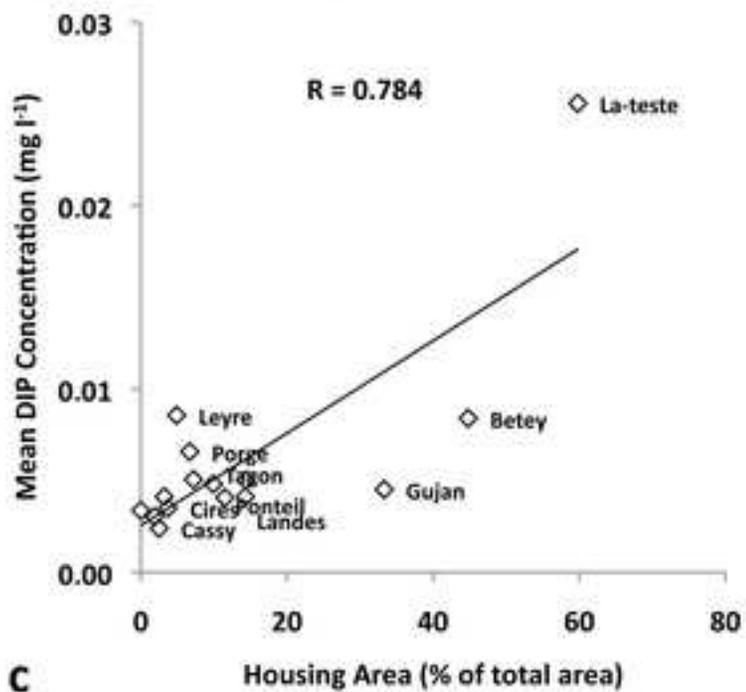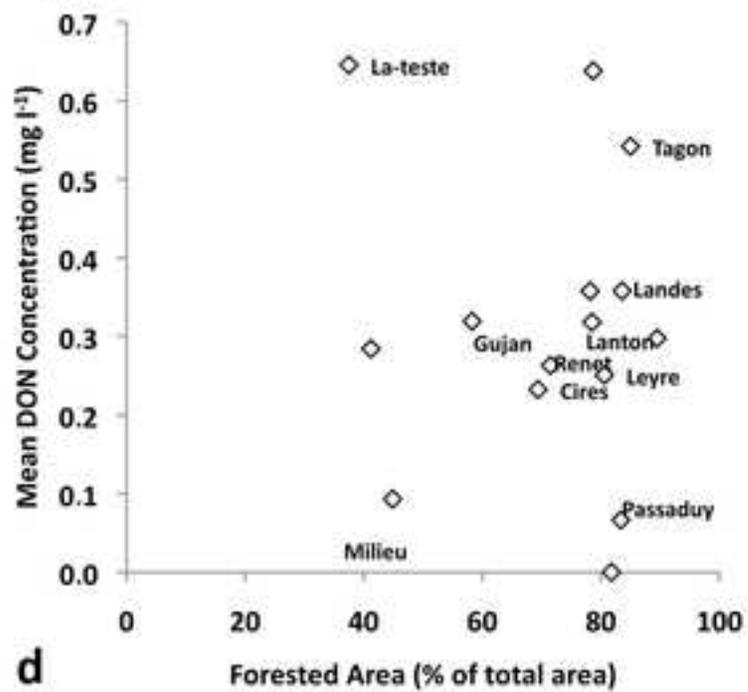
Table 1: Proportion of land use categories in the Arcachon Bay catchment

Name	Aiguemorte	Betey	Cassy	Cires	Gujan	Landes	Lanton	La Teste	Leyre	Milieu	Passaduy	Ponteil	Porge	Renet	Tagon
Area (km^2)	25.6	15.6	22.8	48.7	29.1	87.4	36.1	11.2	2141.3	17.4	21.3	23.3	221.6	17.9	29.6
Farming (%)	0.0	0.0	0.0	17.7	3.4	0.0	7.0	2.7	10.3	51.6	6.1	0.0	0.9	10.7	0.0
Newly deforested (%)	3.3	14.0	19.3	9.2	5.0	2.2	11.2	0.0	4.2	3.6	8.6	6.7	13.7	3.5	5.1
Housing (%)	7.2	44.8	2.5	3.7	33.3	14.3	3.2	59.8	4.9	0.0	1.9	11.5	6.7	14.4	9.9
Forest (%)	89.5	41.2	78.2	69.4	58.3	83.6	78.5	37.5	80.6	44.9	83.4	81.8	78.7	71.5	85.0

Table 2 : Mean nutrient concentrations in streamwater (mg-N and mg-P l^{-1}) in 2007 and 2008. The mean is calculated from two years of survey in 15 catchments.

2007	Aiguemorte	Betey	Cassy	Cires	Gujan	Landes	Lanton	La teste	Leyre	Milieu	Passaduy	Ponteil	Porge	Renet	Tagon
Nitrate mg-N l^{-1}	0.17	0.27	0.24	2.52	1.09	0.11	0.76	0.41	1.50	2.70	1.13	0.27	0.20	0.78	0.32
Ammonium mg-N l^{-1}	0.07	0.08	0.04	0.06	0.19	0.09	0.06	0.30	0.06	0.06	0.02	2.45	0.07	0.07	0.04
DON mg-N l^{-1}	0.29	0.28	0.35	0.24	0.32	0.36	0.32	0.64	0.25	0.10	0.07	-	0.63	0.27	0.55
DIP mg-P l^{-1}	0.005	0.008	0.002	0.003	0.005	0.004	0.004	0.026	0.009	0.003	0.003	0.004	0.007	0.005	0.005
2008															
Nitrate mg-N l^{-1}	-	-	-	4.82	-	0.06	0.91	-	1.99	3.29	-	0.38	0.20	1.37	0.17
Ammonium mg-N l^{-1}	-	-	-	0.06	-	0.06	0.07	-	0.06	0.11	-	1.10	0.13	0.07	0.15
DIP mg-P l^{-1}	-	-	-	0.003	-	0.002	0.008	-	0.006	0.002	-	0.004	0.002	0.006	0.006

Table 3

Table 3: Nutrient fluxes at the 15 river mouths in 2007 and 2008. Nutrient fluxes are calculated from our data. Fm/Fc is the ratio between the measured DIN flux and the modelized DIN flux. The calculation of the modelized flux is based on the surface area of each land-use and the corresponding export rate but it excludes the DIN flux due to urban area because this export rate can't apply to the overall urban area.

2007	Aiguemorte	Betey	Cassy	Cires	Gujan	Landes	Lanton	La Teste	Leyre	Milieu	Passaduy	Ponteil	Porge	Renet	Tagon	Total
Nitrate (10^3 kg-N)	1.0	0.9	1.2	27.0	6.9	2.2	6.0	1.0	707	10.3	5.3	1.3	9.8	3.1	2.1	785
Ammonium (10^3 kg-N)	0.4	0.3	0.2	0.6	1.2	1.6	0.5	0.7	28.2	0.2	0.1	12.5	3.5	0.3	0.3	51
DON (10^3 kg-N)	1.7	1.0	1.8	2.5	2.0	6.9	2.5	1.6	118	0.4	0.3	-	31.0	1.0	3.5	174
DIP (10^3 kg-P)	0.03	0.03	0.01	0.04	0.03	0.08	0.03	0.06	4.03	0.01	0.01	0.02	0.32	0.02	0.03	4.8
DIN Fm/Fc	1.2	0.5	1.1	1.0	0.5	1.2	1.4	0.7	1.0	2.5	0.9	0.1	1.4	1.9	0.7	-
2008																
Nitrate (10^3 kg-N)	-	-	-	46.6	-	1.1	6.5	-	846	11.4	-	1.8	8.7	4.9	1.0	928
Ammonium (10^3 kg-N)	-	-	-	0.5	-	1.1	0.5	-	26.9	0.4	-	5.1	5.6	0.2	0.9	41
DON (10^3 kg-N)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DIP (10^3 kg-P)	-	-	-	0.03	-	0.04	0.06	-	2.64	0.01	-	0.02	0.09	0.02	0.03	2.9
DIN Fm/Fc	-	-	-	1.7	-	0.5	0.8	-	1.2	0.4	-	5.4	0.8	0.8	1.2	-

Table 4: Mean export rates by land-use

	Agriculture	Forest	Deforested area	Urban area
Nitrate kg N km^{-2} year^{-1}	2850	45	93	62
Ammonium kg N km^{-2} year^{-1}		13		Up to100
DIP kg P km^{-2} year^{-1}		0.57		Up to 8.5
DON kg N km^{-2} year^{-1}		63		