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Abstract

Diffuse transfer of nitrogen (N) and phosphorus (P) in agricultural catchments is controlled by the mobilisation of sources and their delivery to receiving waters. While plot scale experiments have focused on mobilisation processes, many catchment scale studies have hitherto concentrated on the controls of dominant flow pathways on nutrient delivery. To place mobilisation and delivery at a catchment scale, this study investigated their relative influence on contrasting nitrate-N and soluble P concentrations and N:P ratios in two shallow groundwater fed catchments with different land use (grassland and arable) on the Atlantic seaboard of Europe. Detailed datasets of N and P inputs, concentrations in shallow groundwater and concentrations in receiving streams were analysed over a five year period (October 2010 – September 2015). Results showed that nitrate-N and soluble P concentrations in shallow groundwater give a good indication of stream concentrations, which suggests a dominant control of mobilisation processes on stream exports. Near-stream attenuation of nitrate-N (-30%), likely through denitrification and dilution, and enrichment in soluble P (+100%), through soil-groundwater interactions, were similar in both catchments. The soil, climate and land use controls on mobilisation were also investigated. Results showed that grassland tended to limit nitrate-N leaching as compared to arable land, but grassland could also contribute to increased P solubilisation. In the context of land use change in these groundwater fed systems, the risk of pollution swapping between N and P must be carefully considered, particularly for interactions of land use with soil chemistry and climate.

Keywords

Agricultural catchments, land use, climate, nutrients, nitrate, phosphorus

1. Introduction:

Land-to-water transfer of nitrogen (N) and phosphorus (P) is a major concern worldwide as excessive concentrations of these two nutrients cause eutrophication in freshwater and marine ecosystems (Conley et al., 2009). Diffuse emissions from agricultural origin can represent a significant contribution to annual N and P loads in rivers (Dupas et al., 2015a).

Mitigation measures to decrease N and P emissions from agricultural landscapes must rely on underpinning research to understand mobilisation and delivery mechanisms in order to be effective and several mechanisms have been identified (Lloyd et al., 2016; Mellander et al., 2012; Outram et al., 2016). It is generally accepted that N is prone to vertical leaching from the soil, through the unsaturated zone down to the saturated zone. It can then be transferred to surface waters, mainly as nitrate, via groundwater (Legout et al., 2007; Mellander et al., 2014; Molenat et al., 2008). Nitrate mobilised below the rooting zone may be subject to denitrification, which generally takes place within anoxic groundwaters, riparian wetlands and the hyporheic zone (Anderson et al., 2014; McAleers et al., 2017; Oehler et al., 2007). Mobilised nitrate may also have long time lags between mobilisation and emergence, due to the potentially long transit time of water in the unsaturated and saturated zone (Fovet et al., 2015; Hrachowitz et al., 2010). Phosphorus has a higher adsorption affinity with the soil compared to nitrate; as a result it is less soluble and is less prone to leaching. A general understanding is that P is typically transferred to surface waters via surface pathways, either in soluble or particulate form (Sharpley et al., 2008). However, several studies have highlighted the possibility of soluble P leaching into shallow groundwater and subsequent lateral transfer to surface water as a dominant mechanism in groundwater-fed catchments (e.g. Dupas et al., 2015c; Haygarth et al., 1998; Holman et al., 2010; Mellander et al., 2016; van der Salm et al., 2011).

Nitrate and soluble P leaching is controlled by several factors, some of which are manageable and some of which are inherent properties of soils and climate. Nitrate leaching is controlled by i) the balance between fertiliser inputs and crop uptake on an annual basis; ii) soil mineralisation, which increases when the soil C:N ratio is low and when favourable moisture and temperature conditions are met (Rodrigo et al., 1997); iii) temporal mismatches between crop uptake capacity and high nitrate concentration in the soil combined with high drainage potential (particularly in autumn, Dupas et al., 2015d). In temperate regions, grasslands have been shown to have a better capacity to take up N from the soil throughout the year, particularly in the autumn period, compared to cropland (McDowell et al., 2014; Moreau et al., 2012), although urine patches in grazed grassland can be hotspots of nitrate leaching.

Soluble P leaching is controlled by i) the soil P content, as determined by soil P tests; ii) soil chemistry, particularly the abundance of iron (Fe) and aluminium (Al) oxides, which are important adsorption sites in acidic soils (Daly et al., 2015; Schoumans and Chardon, 2015); iii) temporal variation of soil pH, redox state (Henderson et al., 2012) and drying-rewetting or freezing-thawing cycles (Blackwell et al., 2010); iv) organic matter (OM) content, which may control the formation of Fe-bound organic P colloids that are more mobile than truly soluble P (Granger et al., 2007), and which influences the concentration of dissolved organic matter (DOM) that can compete with P for adsorption sites (Kang et al., 2009); v) land use, particularly the presence of grassland, which is often associated with high OM content in soil and which may release root exudates that stimulate the microbial biomass and bring P into solution (Roberts et al., 2013). Grassland may also favour preferential flow paths through macropores, enhancing nitrate and soluble P transport (Djodjic et al., 2004; Gachter et al., 1998).

Several studies comparing the export behaviour of N and P in agricultural catchments along the Atlantic seaboard of Europe have highlighted the crucial role played by dominant flow pathways on export patterns (e.g. Lloyd et al., 2016; Mellander et al., 2012; Outram et al., 2016). In general, well-drained catchments are prone to nitrate leaching and subsequent transfer via groundwater, whereas poorly-drained catchments can transfer large masses of P via surface flow pathways (Jordan et al., 2012; McDowell et al., 2014). However, few studies have compared catchments with similar dominant flow pathways to investigate the role of mobilisation and delivery mechanisms at this small catchment scale.

The main aim of this paper, therefore, was to investigate mobilisation processes (i.e. leaching) as an important role in the transfer continuum of nitrate-N and soluble P in groundwater-fed catchments. This was undertaken by monitoring the nutrient transfer continuum, from source to mobilisation and from mobilisation to delivery (Haygarth et al., 2005), in two intensively studied agricultural catchments (with similar groundwater fed systems) on the Atlantic seaboard of Europe. A detailed survey of N and P input and content in soil was used to characterise the sources, nitrate-N and soluble P concentration in shallow groundwater was used to characterise the amount of nutrient being mobilised below the rooting zone and comparison of groundwater and stream nitrate-N and soluble P concentration was used to characterise delivery. The specific objectives were to i) investigate the respective influence of mobilisation and delivery mechanisms on contrasting nitrate-N and soluble P concentrations and N :P ratios in the two catchments and ii) analyse the respective controls of soil properties, climate and land use on nitrate-N and soluble P mobilisation. We use this analysis to explore some implications for the future trajectory (i.e. evolution under changing external forces) of diffusion pollution in these and similar catchment types under land use and climate change scenarios.

2. Materials and methods

2.1. Study areas

This investigation took place in two intensively farmed catchments in the pedo-climatic zone of the Atlantic seaboard of Europe, in Western France and South-western Ireland (Fig. 1).

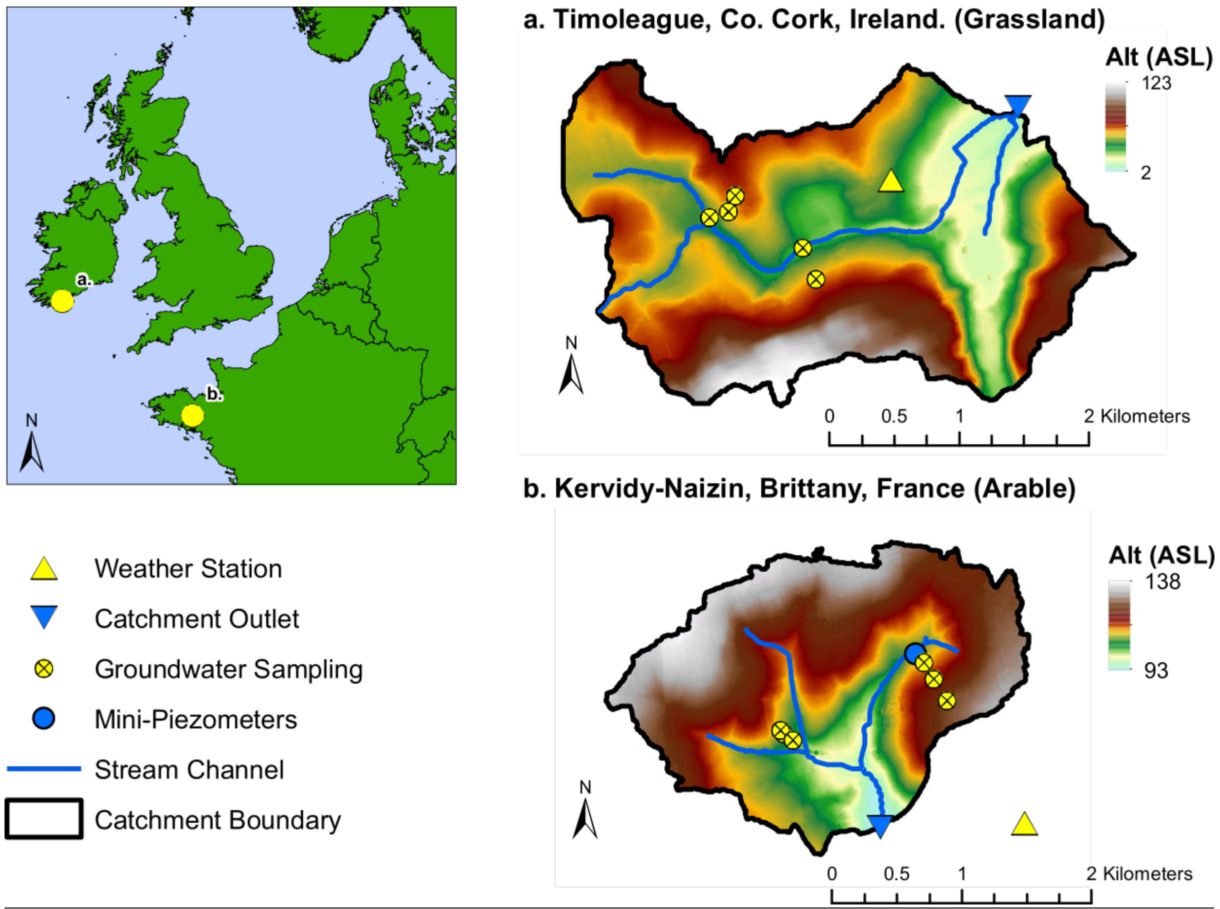


Figure 1: Catchment site map. Location of the Timoleague catchment in Ireland and the Kervidy-Naizin catchment in France and location of the monitoring sites.

The French catchment, Kervidy-Naizin, belongs to the AgrHyS environmental research observatory, where the impacts of agriculture and climate change on water quality are studied (Aubert et al., 2013). Kervidy-Naizin is a 5 km² catchment drained by a stream of second Strahler order. Climate is temperate oceanic, with mean ± standard deviations of annual rainfall, temperature and discharge of 938 ± 218 mm, 11.3 ± 0.5 °C and 359 ± 206 mm, respectively (October 2010 – September 2015). Topography is gentle, with an elevation range of 93-135 m above sea level. The bedrock consists of impervious, locally fractured Brioverian schists and is capped by several metres of unconsolidated weathered material and silty, loamy soils. The hydrological behaviour is dominated by the development of a water table that varies seasonally along the hillslope. In the upland domain, consisting of well-drained soils (86% of the catchment area), the water table remains below the soil surface throughout the year, varying in depth from 1 m to more than 8 m. In the wetland domain, developed near the stream and consisting of hydromorphic soils (14% of the catchment area), the water table is shallower, remaining near the soil surface generally from October to April each year (Molenat et al., 2008). Artificial drainage represents <10% of the surface area but is generally ineffective at lowering the water table in the wetland area because the drains are in disrepair. The baseflow index (Institute of Hydrology, 1980) during the October 2010 – September 2015 study period was 0.7. The land use is mostly agriculture, specifically arable crops and confined animal production (dairy cows and pigs). A farm survey conducted in 2013 led to the following land use zones: 71% winter cereals and maize, 16% grassland and 13% other crops (rape seed, vegetables). Soil tillage (10 cm to 40 cm) is practised for all crops (including temporary grassland) one to three times a year; cultivation primarily takes place in spring for summer crops and autumn for winter crop; all fields are ploughed every one to three years. Annual nutrient inputs were typically (on average for the crop rotation present in 2013, i.e., for a 1 to 5 year period) 212 kg N ha^{-1} (71% organic, 29% chemical) and 62 kg P ha^{-1} (83% organic, 17% chemical). Direct inputs from grazing livestock were included in the organic N and P input term, and atmospheric deposition primarily comes from fertiliser volatilisation, thus it was not included in the N input term to avoid double-counting. Pig slurry dominates organic effluent application, followed by cow manure; spreading period stretches from February to May and organic effluent application is prohibited from July to January (March for maize).

The Irish catchment, Timoleague, is part of the Agricultural Catchment Programme, which is a European Union Nitrates Directive evaluation experiment established to monitor agricultural practices under water quality policies in Ireland (Wall et al., 2011). Timoleague is a 7.6 km² catchment drained by a stream of second Strahler order. Climate is temperate oceanic, with mean ± standard deviations of annual rainfall, temperature and discharge of 1047 ± 92 mm, 10.1 ± 0.5 °C and 589 ± 106 mm, respectively (October 2010 – September 2015). The topography is rolling to flat with an elevation range of 17-127 m above sea level.

The lithology consists of Old Red Sandstone and mudstone of the Castlehaven formation. Belowground flow paths are likely concentrated in the high permeability layers and along the contacts of different layer types and in possible fractures or faults. The aquifer is unconfined and classified as productive with a secondary permeability. In the upland domain, consisting of well-drained brown earths (Cambisols 87% of the catchment area), the water table remains below the soil surface throughout the year, varying in depth from 2 m to more than 10 m. In the wetland domain, developed near the stream and consisting of poorly drained Gleysols, alluvials and peat soils (13% of the catchment area), the water table is shallower, remaining near the soil surface generally from October to April each year (Mellander et al., 2014). The baseflow index (Institute of Hydrology, 1980) during the October 2010 – September 2015 study period was 0.7. According to the Irish Soil Information System the soil texture is primarily loam. The land use is mainly dairy production with an average livestock density of 1.9 livestock units (LU) ha^{-1}. The animals are housed over winter and graze over the spring to autumn period. The surface area is represented by 77% grassland and 11% mixture of cereals (e.g. spring barley, spring wheat and winter oilseed rape), forage maize and root crops (e.g. fodder beet). Based on 2010 and 2011 nutrient use census, the average annual input rates were approximately 310 kg N ha^{-1} (41% organic and 59% chemical) and 54 kg P ha^{-1} (92% organic, 8% chemical). As in the Kervidy-Naizin catchment, direct inputs from grazing livestock were included in the organic N and P input term, and atmospheric deposition was not included. Timings of these fertiliser inputs were mainly skewed to spring, when growth demands were highest, as 73% of N and 75% of P was applied by the end of June. Peak application rates (average 60kg N ha^{-1} and 24 kg P ha^{-1} in the available organic form and 51 kg N ha^{-1} and 2 kg P ha^{-1} in the mineral form) were in April, which is required at this time to match the nutrient demand as grass growth typically peaks in Ireland during this period.

2.2. <u>Soil, stream and groundwater monitoring</u>

In the Kervidy-Naizin catchment, soil samples were taken using a triangular network sampling method at 89 sampling points in 2013 (Matos-Moreira et al., 2017). Seven soil cores (0-15 cm) were taken within a 1 m radius around each of the 89 sampling point and were composited. Samples were air-dried, sieved (2 mm mesh) and stored at room temperature before analysis. Dyer P was determined by using 20 g l^{-1} citric acid with a soil:solution ratio of 1:5 (NF X 31-160). Oxalate extractable Al and Fe were determined after extraction with 0.0866 mmol l^{-1} oxalic acid + 0.1134 mmol l^{-1} ammonium oxalate using a soil:solution ratio of 1:40 (w:v), in the dark and at pH 3 (Tamm, 1922). Organic matter, nitrogen, and carbon contents were determined by dry combustion (1000°C, NF ISO 13878, NF ISO 10694).

Also in the Kervidy-Naizin catchment, stream discharge was measured every minute at a gauging station with a float operated sensor upstream of a rectangular weir and a data logger (OTT Thalimedes). The weather station (Cimel Enerco 516i) was located 1.1 km from the catchment outlet (Fig. 1b) and recorded hourly rainfall and temperature. The stream chemical monitoring consisted of a daily sampling performed manually at approximately the same time (17:00 local time). For each sample, two aliquots were filtered directly on-site for nitrate-N analysis (0.22 µm) and soluble reactive P (SRP) analysis (0.45 µm). Nitrate was determined as N by ionic chromatography (DIONEX DX 100), with a precision of ± 2.5%. Soluble reactive P was determined colorimetrically by reaction with ammonium molybdate, with a precision of ± 0.004 mg l^{-1}. For SRP, samples were analysed every 6 days from October 2010 to September 2013 and every day (i.e., like nitrate) from October 2013 to September 2015 (Minaudo et al., in review). Other N and P species were not considered in this study because they represent minor fractions of dissolved N and P: nitrite and ammonium concentrations determined in grab samples were generally below the detection limits, respectively < 0.07 mg l^{-1} and < 0.04 mg l^{-1} (n=147, unpublished data). Soluble reactive P represented >80 % of total dissolved P (n=25, Dupas et al., 2015b).

Shallow groundwater samples were collected every 3 - 4 months in 10 wells along two transects (Fig. 1b). Screening depths were 1.5 – 3 m for the wells located downslope and 4 – 8 m or 6 – 10 m for those upslope, i.e. in the groundwater fluctuation zone. At these depths, groundwater is typically aerobic, poor in organic compounds or other electron donors, limiting significant denitrification (Molénat et al., 2002). This is in contrast to deeper pathways, whereby anaerobic conditions promote the dissolution of solid phase bacterial energy sources ($Mn^{2+,}$ Fe^{2+}, S^{-}), which can in turn drive autotrophic denitrification (Pauwels et al., 1998). A shallow groundwater comparison is therefore appropriate to characterise nitrate mobilisation (i.e. leaching) rather than nitrate reduction (i.e. denitrification) processes (McAleer et al., 2017). Only nitrate-N was analysed in the groundwater samples. Soluble reactive P was not investigated in these wells because it was assumed to be low in this catchment. To test the latter assumption and to investigate SRP mobilisation below the rooting zone, one shallow piezometer (screening depth = 1 m) was placed at the footslope of one transect; it was sampled weekly during the 2013-2014 water year.

Finally, the Kervidy-Naizin catchment was equipped with mini-piezometers placed within the soil in triplicate (screening depth: 4 – 5 cm) in two adjacent plots in a cropland field and a grassland plot. The mini-piezometers were made from 15 cm Polyvinyl chloride tubes (diameter = 5 cm) closed at the bottom, with three slits at 4 cm, 4.5 cm and 5 cm below the soil surface. These mini-piezometers were sampled with a syringe, five times during the 2013-2014 water year, when water was present in the mini-piezometers (from January to March). Samples were analysed for SRP to compare the effect of land use on SRP mobilisation with similar land and climate characteristics.

In the Timoleague catchment, soil samples were taken using a regular grid sampling scheme at 27 sampling points in 2012. As in the Kervidy-Naizin catchment, a grid sampling scheme was chosen to cover the variability of factors influencing soil properties (such as soil classification, land use and topography). Forty soil cores (0-10 cm) were taken from a 25 m x 25 m area around each sampling point and composited. Samples were oven-dried (40°C), sieved (2 mm mesh) and stored at room temperature before analysis. Influence of oven-drying of Timoleague soils as compared to air-drying of Kervidy-Naizin was assumed to have a minor influence on subsequent analyses given the low temperature used. A modified Mehlich (Mehlich, 1984) method was used to extract P, Al and Fe from a 2 g sub-sample of soil with Mehlich3 (M3) reagent (0.2 M CH_3COOH + 0.25 M NH_4NO_3 + 0.015 M NH_4F + 0.13 M HNO_3 + 0.001 M EDTA) at a 1:10(w/v) soil to solution ratio for 5 min. According to Sarr et al. (2007), this method extracts 1.5 times less P from the soil than the Dyer method used in the Kervidy-Naizin catchment. Organic matter was estimated as the loss-on-ignition from 4 g soil sub-samples (500 °C for 16h). Total carbon and N were determined by dry combustion using a CN LECO FP2000 analyser (LECO Corporation, St. Joseph, MI, USA),

In the Timoleague catchment, stream discharge was measured every 10 minutes with a vented-pressure instrument (OTT Orpheus Mini) installed in a stilling well adjacent to non-standard Corbett flat-v weirs. The weather station (Campbell Scientific BWS200) was located in the central part of the catchment (Fig. 1a) and recorded rainfall and temperature on a 10 min basis. For both catchments, daily mean values of discharge and weather data are presented. Also in Timoleague, the river outlet was equipped with bankside analysers that monitored total oxidized nitrogen (TON) and total reactive P (TRP) concentrations. TON was measured in situ by a UV probe (Hach-Lange Nitratax), with a measuring range of 0.1 – 50 mg l^{-1}. It was assumed that TON was equivalent to nitrate-N (Melland et al., 2012). The P instrumentation (Hach-Lange Phosphax-Sigma) measured TRP every 20 min by colorimetry using the molybdate–antimony method (DIN EN ISO 6878), with a measuring range of 0.01 – 5 mg l^{-1} (Wall et al., 2011). It was also assumed that TRP was approximately equivalent to SRP since the flow-weighted mean SRP was previously reported to account for 98–99% of the flow weighted mean TRP in another (similar groundwater-fed) Irish grassland catchment (Shore et al., 2014). Similar to the Kervidy-Naizin catchment, nitrite and ammonium concentrations determined in grab samples were low, respectively 0.023 ± 0.003 mg l^{-1} and

0.183 ± 0.017 mg l^{-1} (n=256 and 298, unpublished data). Soluble reactive P represented >70 % of total dissolved P (n=187, unpublished data).

Groundwater was sampled monthly in six multilevel monitoring wells along two transects (Mellander et al., 2014; McAleer et al., 2017; Fig. 1a). The wells consisted of three piezometers that screened different depths; only the piezometers that screened comparable depths to the arable catchment (i.e. in the groundwater fluctuation zone: 2.8 – 5.5 m for the wells located downslope and 5.5 – 12 m for those upslope) were considered here. All samples were filtered immediately after sampling (0.45 µm) and analysed for nitrate-N and SRP.

2.3. Data analysis

This analysis focuses on the dissolved N and P form because previous studies have shown that particulate transfer involved different mechanisms from the input-groundwater-stream continuum investigated here, e.g. stream bank erosion, surface runoff, etc. (Dupas et al., 2015b; Sherriff et al., 2015). Despite the monitoring protocols differing slightly between the two catchments, it was possible to extract similar metrics from each, and perform a comparison of the factors controlling nitrate-N and soluble P mobilisation and delivery, based on the following assumptions and data treatments:

- It was assumed that the soil sampling protocols were comparable in both catchments. Because tillage > 15 cm was performed at least once a year in each field in the Kervidy-Naizin catchment, which homogenises the soil properties over this depth, a soil sampling depth of 10 cm in Timoleague and 15 cm in Kervidy-Naizin can be compared.
- Based on previous studies, it was assumed that TON and nitrate-N were comparable (Melland et al., 2012) and that TRP and SRP were similarly comparable (Shore et al., 2014).

- Sub-hourly stream data from the Timoleague catchment were averaged every hour and then sub-sampled at the time of sampling in the Kervidy-Naizin catchment (17:00 local time) to standardise the time-series between the catchments.
- Average (± standard deviations) values were considered for groundwater data as differences between catchments were larger than spatial variability within each catchment. For comparison of nitrate-N concentrations, five upslope piezometers were selected in the Kervidy-Naizin catchment and three upslope piezometers were selected in the Timoleague catchment. The reason for excluding downslope piezometers was because they were placed in vegetated buffer strips in the Kervidy-Naizin catchment (whereas this study aimed to investigate mobilisation below cropland fields in this catchment) and also placed in denitrifying riparian zones in both catchments (whereas this study aimed to investigate mobilisation prior to riparian attenuation). For comparison of SRP concentrations, one shallow piezometer placed below the rooting zone at the footslope of a cropland field was selected in the Kervidy-Naizin catchment and five piezometers located at similar topographic positions were selected in the Timoleague catchment. The piezometers selected were representative of each catchment in the sense that they were placed in cropland fields in Kervidy-Naizin and in grassland fields in Timoleague, and they had similar screening depths and topographic positions along the hillslopes.

The data analyses were fourfold:

- Comparing the inter- and intra-annual variability of hydroclimatic variables and nitrate-N and soluble P loads in the two catchments. Annual nitrate-N and soluble P loads (L) were estimated with the discharge-weighted concentration method (Moatar et al., 2013):

$$\mathrm{L} = K * \left(\frac{\sum_{i=1}^{n} C_i * Q_i}{\sum_{i=1}^{n} Q_i} \right) * \bar{Q}$$

where C_i is the instantaneous nitrate-N or soluble P concentration, Q_i is the mean daily discharge associated with C_i, $\overline{Q}$ is mean annual discharge, K is a conversion factor to obtain load in kg ha^{-1} yr^{-1} and n represents the number of (C_i, Q_i) pairs for each water year .

- Comparing time-weighted nitrate-N and soluble P concentrations in groundwater and flow-weighted nitrate-N and soluble P concentrations in stream water between the two catchments. In addition, variability in concentration and discharge data was quantified using the coefficient of variation, defined as the ratio of the standard deviation to the mean. This metric has been used in previous studies to characterise the chemodynamic or chemostatic character of solute export (according to the relative dispersion of concentration data compared to discharge; Musolff et al., 2015). The coefficient of variation was calculated both on an annual mean and daily basis, to describe both inter-annual and intra-annual variability.
- Calculating N:P ratios for fertiliser inputs, groundwater concentrations and stream flow-weighted concentrations to investigate the respective control of the sources, the mobilisation mechanisms and delivery on contrasting nitrate-N and soluble P concentrations and load in the two catchments. To relate groundwater and stream concentrations to current inputs (averaged over a five year period) we assumed steady state conditions in the two catchments, which is acceptable here as transit times are < 10 years in both catchments and there has been no major change in land use and/or N and P inputs in the recent period (Molenat et al., 2008).
- Comparing soil, land use and climate characteristics to investigate their respective effect of nitrate-N and soluble P mobilisation/leaching.

All graphical figures and statistical tests were performed with SigmaPlot (Systat Software, San Jose, CA). Unless stated otherwise, two-tailed t-tests were employed for comparisons, and normal distributions were checked using a Shapiro-Wilk test.

3. Results and discussion

3.1. Temporal variability in the hydroclimate, nitrogen and phosphorus loads

The Kervidy-Naizin and the Timoleague catchments appeared to be affected by similar seasonal weather patterns but different inter-annual weather patterns. Both catchments were characterised by mild temperatures and the occurrence of rainfall throughout the year (Table 1; Fig. 2 a and b); mean annual temperature was slightly but significantly higher in Kervidy-Naizin (11.3 ± 0.5 °C versus 10.1 ± 0.5 °C, $p < 0.05$) but the annual cumulated rainfall was not significantly different in both catchments (938 ± 218 mm in Kervidy-Naizin versus 1047 ± 92 mm in Timoleague, $p > 0.05$). In both catchments, stream discharge showed a strong seasonality with high flow during the winter period and, for the most part, low flow during summer. In the Timoleague catchment, the stream flowed throughout the year while the stream was dry during one to two months in the summer period every year in the Kervidy-Naizin catchment (Fig. 2c and 3a). This difference is due to higher summer evapotranspiration in Kervidy-Naizin (3.7 ± 0.3 mm day^{-1} versus 2.7 ± 0.3 mm day^{-1} from June to August, $p < 0.05$) and higher summer rainfall in Timoleague (3.2 ± 1.2 mm day^{-1} versus 1.8 ± 0.6 mm day^{-1} from June to August, $p < 0.05$). Annual discharge was on average lower, but more variable, in the Kervidy-Naizin catchment than in the Timoleague catchment (359 ± 206 mm versus 589 ± 106 mm); the larger inter-annual variability in the Kervidy-Naizin catchment is reflected by the larger estimated coefficient of variation (57% versus 18%).

[Please insert Table 1 here]

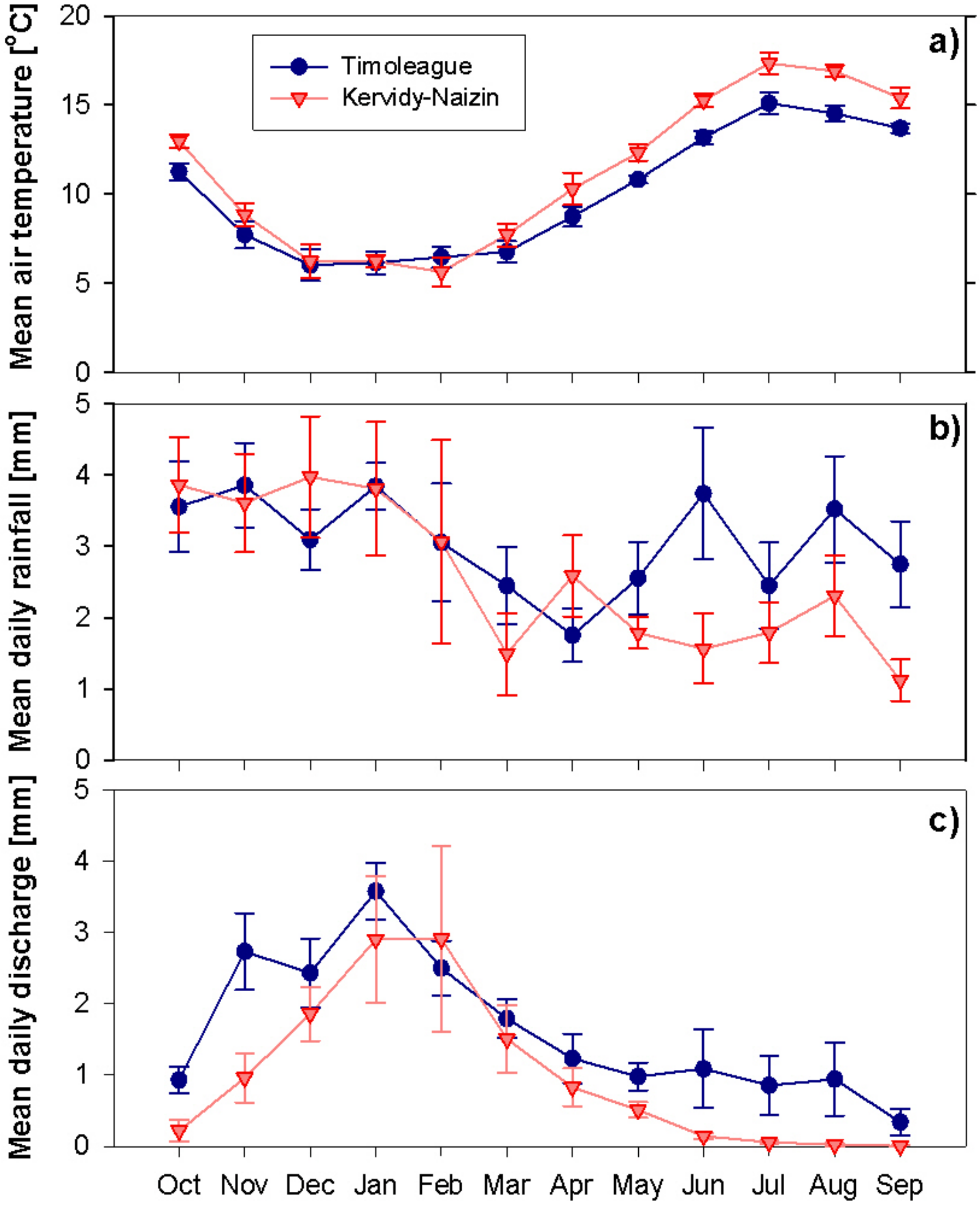


Figure 2: Monthly averaged air temperature (a), daily rainfall (b) and discharge (c) over the period October 2010 – September 2015 in Timoleague and Kervidy-Naizin catchments. Error bars represent one standard deviation (n = 5 years).

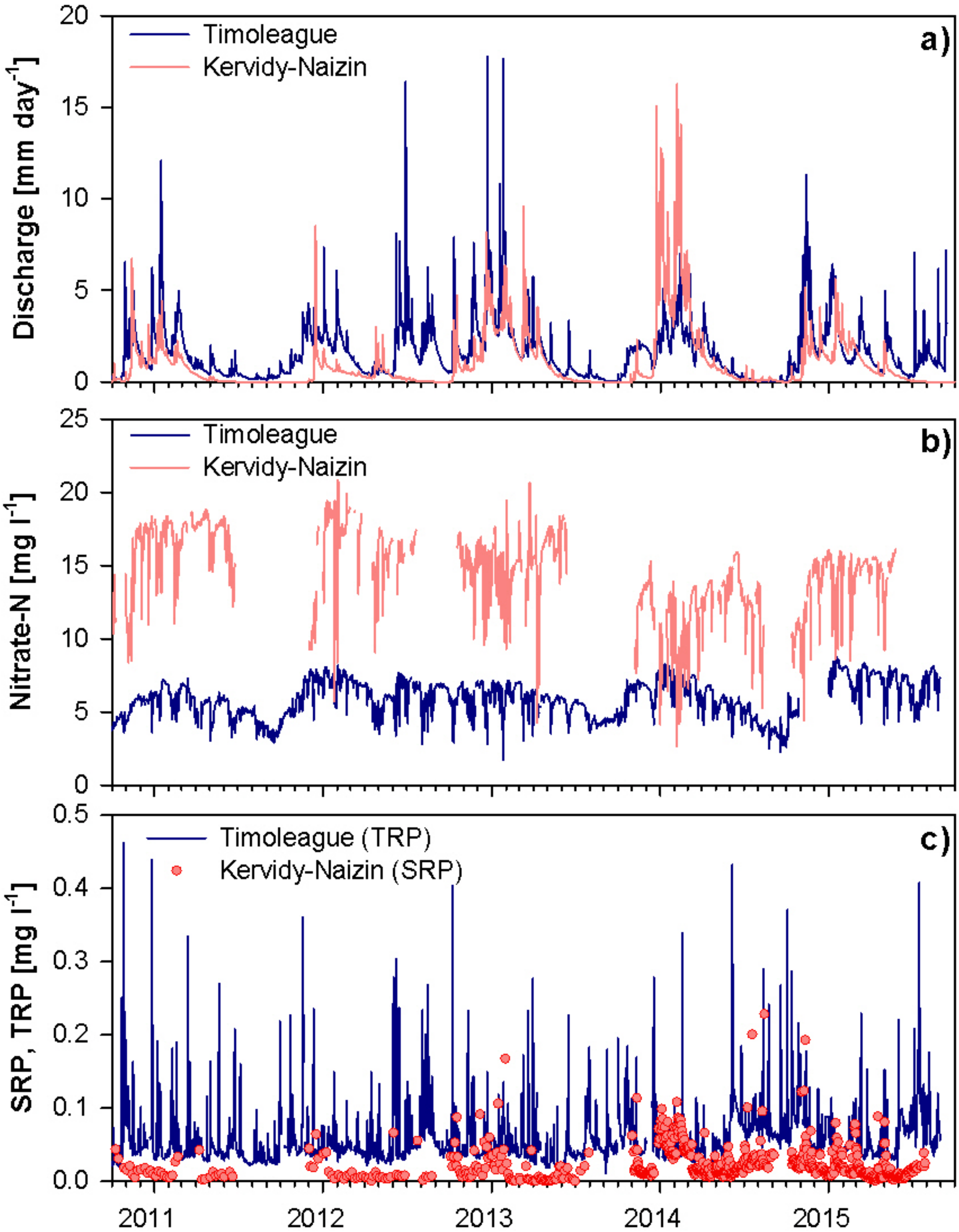


Figure 3: Time series of daily discharge (a), nitrate concentration (b), and soluble phosphorus concentrations (c) at the outlet of Timoleague and Kervidy-Naizin catchments. Soluble phosphorus concentration in Kervidy-Naizin was only measured on a 6 day frequency from October 2010 to September 2013 and every day from October 2013 to September 2015.

Annual soluble P loads were, on average, also higher in the Timoleague catchment (0.39 ± 0.09 kg TRP ha^{-1} yr^{-1} versus 0.13 ± 0.13 kg SRP ha^{-1} yr^{-1} in the Kervidy-Naizin catchment), but annual nitrate-N loads were on average higher in the Kervidy-Naizin catchment (46 ± 20 kg N ha^{-1} yr^{-1} versus 37 ± 7 kg N ha^{-1} yr^{-1} in the Timoleague catchment). Similar to annual discharge, nutrient annual loads were more variable in the Kervidy-Naizin catchment than in the Timoleague catchment (Fig. 4); this is reflected by the larger estimated coefficient of variation in the Kervidy-Naizin catchment (43% versus 20% for nitrate-N load and 103% versus 23% for soluble P load). Only the difference between soluble P annual loads was statistically significant for the five years of study ($p < 0.05$, $n = 5$). Flow-weighted mean annual soluble P concentration was significantly higher in the Timoleague catchment (66.6 ± 7.2 µg P l^{-1} versus 29.3 ± 15.8 µg P l^{-1} in the Kervidy-Naizin catchment, $p < 0.05$, $n = 5$) while flow-weighted mean annual nitrate-N concentration was significantly higher in the Kervidy-Naizin catchment (13.7 ± 2.5 mg N l^{-1} versus 6.2 ± 0.6 mg N l^{-1} in the Timoleague catchment, $p < 0.05$, $n = 5$). In both catchments, the coefficients of variation estimated for flow-weighted mean annual concentration were lower than that for annual discharge: 53% and 11% for soluble P in Kervidy-Naizin and Timoleague, respectively; and 18% and 10% for nitrate-N in Kervidy-Naizin and Timoleague respectively. The lower variability of concentrations as compared to discharge reveals a biogeochemical stationarity in these catchments, also termed chemostasis (Basu et al., 2010). This chemostatic character observed in many managed catchments worldwide has been previously attributed to the legacy of anthropogenic N and P inputs accumulated within the catchments (Basu et al., 2010; Musolff et al., 2015).

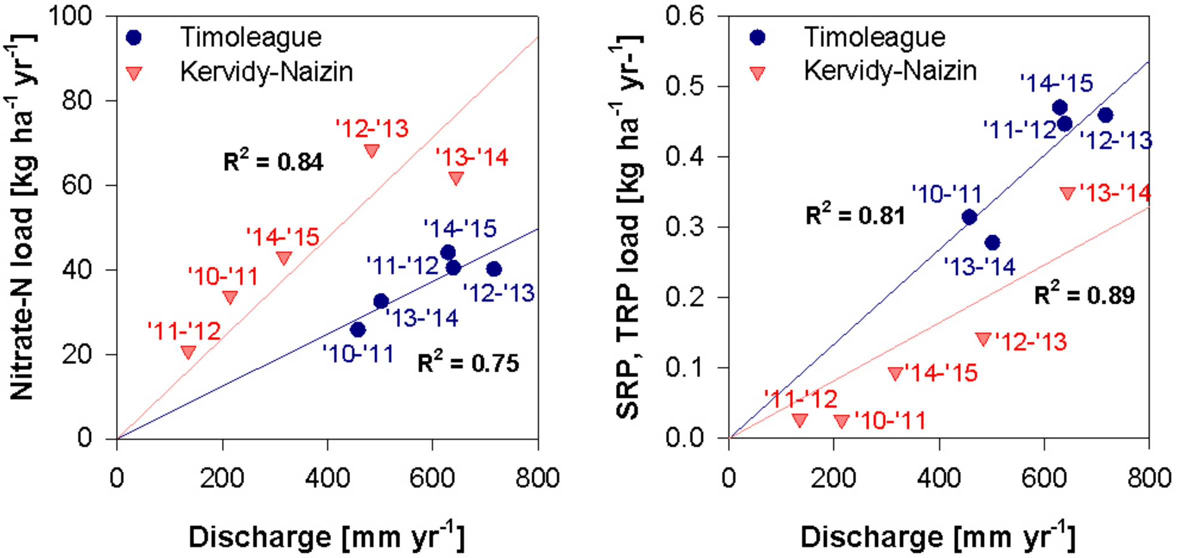


Figure 4: Total annual nitrate (a) and soluble phosphorus (b) loads versus total annual discharge for Timoleague and Kervidy-Naizin catchments. The slope coefficients are significantly different from zero ($p < 0.05$).

The positive linear relationship between annual discharge and nitrate-N and soluble P loads showed that, on an annual basis, exports from the two catchments were transport-limited processes (Basu et al., 2010; Mellander et al., 2014; Molénat et al., 2008; Musolff et al., 2015). The transport limitation evidenced from annual discharge – annual load plots is consistent with the chemostatic character of the catchment, because both transport limitation and chemostasis imply large nutrient storage within the catchments. The slope of the discharge-load relationship was steeper in the Kervidy-Naizin catchment for nitrate-N and steeper in the Timoleague catchment for soluble P, which reflects the contrasting flow-weighted mean concentrations. The transport limitation evidenced from annual loads and the difference in slopes between the two catchments imply larger nitrate-N storage in Kervidy-Naizin and larger storage of mobile P in the Timoleague catchment, which was confirmed by groundwater concentrations presented in Fig. 5 (mean concentrations: 20.8 mg N l^{-1} versus 8.5 mg N l^{-1}, and 12.4 µg P l^{-1} versus 33.1 µg P l^{-1} in Kervidy-Naizin and Timoleague, respectively). The storage of nitrate-N and soluble P in the aquifers, i.e. “anthropogenic legacy of accumulated nutrient sources” (Basu et al., 2010), is likely the result of long term leaching processes from the soil (Musolff et al., 2015). As expected, groundwater concentrations were relatively stable in time, because they integrate nutrient leaching from several fields within the hillslopes where the piezometer transects were located, and because they integrate the response of cropping systems over multiannual time scales. An exception to these stable groundwater concentrations was observed in the nitrate-N time series in the Timoleague catchment, which exhibited higher concentration than usual during the autumn 2010 - autumn 2011 period (Fig. 5a). A previous study showed that this was the result of grassland ploughing and reseeding in the vicinity of a monitored piezometer (Mellander et al., 2014), and the effect of this management operation appeared visible until mid-2013. In contrast, groundwater nitrate-N and soluble P dynamics in the Kervidy-Naizin catchment and soluble P dynamics in the Timoleague catchment could not be related to known management events.

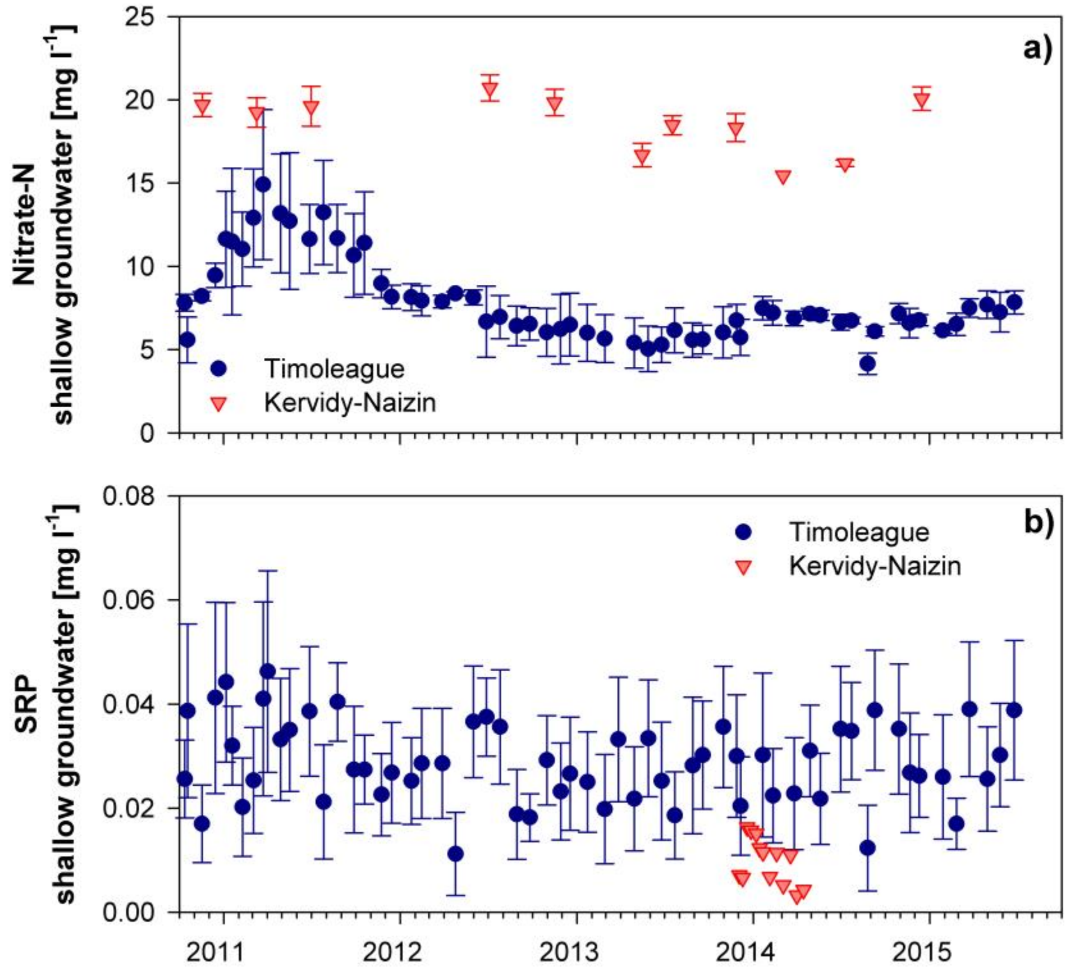


Figure 5: Time series of nitrate (a) and soluble phosphorus (b) concentration in groundwater in Timoleague and Kervidy-Naizin catchments. Nitrate concentrations were measured in upslope piezometers (n=3 in Timoleague and n=5 in Kervidy-Naizin). Soluble phosphorus concentrations were measured in downslope shallow piezometers (n=5 in Timoleague and n=1 in Kervidy-Naizin). Error bars represent one standard deviation.

On a daily basis, the coefficients of variation for soluble P concentration (109% in Kervidy-Naizin and 76% in Timoleague) and nitrate-N concentration (20% in Kervidy-Naizin and 22% in Timoleague) were lower than for discharge (173% in Kervidy-Naizin and 102% in Timoleague), similar to observations of annual mean discharge and concentration. All coefficients of variation calculated on a daily basis were higher than those calculated on an annual basis, most likely because intra-annual weather variability is larger than inter-annual weather variability. Also on a daily basis, an inflexion in the discharge-load relationship indicates a degree of supply-limitation for nitrate-N when daily discharge exceeded approximately 6 mm d^{-1} in both catchments (Fig. 6 a and b). In contrast, the discharge-load plots showed an increase in soluble P supply when daily discharge exceeded approximately 6 mm d^{-1} in the Kervidy-Naizin catchment, and a large variation in the Timoleague catchment (Fig. 6 c and d). This change in discharge-loads relationship when discharge exceeded 6 mm d^{-1} may be explained by the increasing activity of shallow and overland flow pathways during storm events, which connect compartments of the catchment rich in soluble P and poor in nitrate-N (Heathwaite and Dils, 2000). It is a primary cause of the dilution events observed in the nitrate-N time series and the accretion events observed in the soluble P time series for both catchment (Fig. 3 b and c).

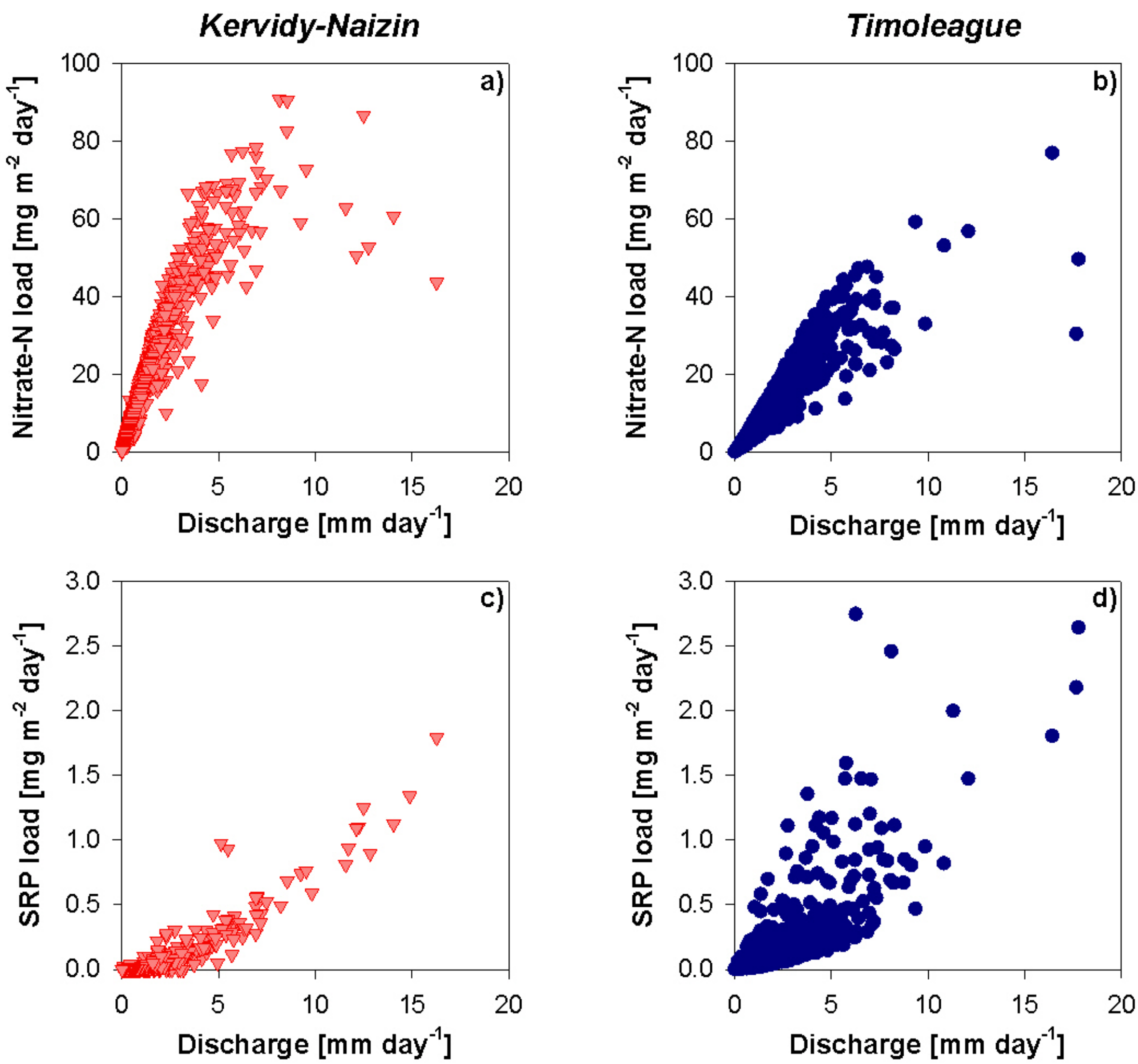


Figure 6: Daily nitrate (a, b) and soluble phosphorus (c, d) loads versus daily discharge for Timoleague and Kervidy-Naizin catchments.

3.2. <u>Nitrogen and phosphorus monitoring along the nutrient transfer continuum</u>

Nitrogen chemical and organic inputs were 46% higher in the Timoleague catchment compared to the Kervidy-Naizin catchment, but flow-weighted mean nitrate-N concentration in the stream was 61% lower. Additionally, P chemical and organic inputs were 15% higher in the Kervidy-Naizin catchments, but flow-weighted mean soluble P concentration was 60% lower. Thus there was no direct relationship between nutrient total inputs and exports in soluble forms. Similar to P inputs, soil P content was higher in the Kervidy-Naizin catchment than in the Timoleague catchment: the average Dyer P in the former was 265.2 mg P kg^{-1} and the average Mehlich 3 P in the latter was 76.4 mg P kg^{-1}, i.e. approximately 114.6 mg P kg^{-1} Dyer P, considering that the Mehlich 3 method extracts 1.5 times less P than the Dyer method (Sarr et al., 2007). Thus the discrepancy previously observed between P sources and P exports was still valid if the soil P content is considered a source factor in addition to P inputs.

This discrepancy between nutrient inputs and soluble exports was further highlighted by N:P ratios. The N:P ratio of inputs was 1.7 times higher in the Timoleague catchment compared to the Kervidy-Naizin catchment, while the N:P ratio of soluble exports in the stream was 6.4 times lower (Fig. 7). However, the decrease in the N:P ratio between groundwater and the stream was similar in both catchments, by a factor of 3.6 and 2.7 in the Kervidy-Naizin and the Timoleague catchments, respectively. This reflected a decrease of nitrate-N concentration by 34% and 27%, respectively, between the groundwater and the river and an increase of soluble P concentration by 136% and 101%.

In summary, the catchment with the highest nitrate-N concentration in the groundwater also had the highest nitrate-N concentration in the stream, but a lower rate of N inputs, and similarly the catchment with the highest soluble P concentration in the groundwater also had the highest soluble P concentration in the stream, but a lower rate of P input. Therefore, no direct relationship could be evidenced between nutrient inputs and exports in soluble form. The decrease in nitrate-N concentration between groundwater and the stream might be explained by attenuation processes such as dilution in non-fertilised near-stream areas and/or denitrification within riparian wetlands and the hyporheic zone (Anderson et al., 2014; Oehler et al., 2007). The increase in soluble P concentration between the groundwater and the stream might be explained by additional transfer to the river via overland flow and/or via the interception of shallow groundwater with the soil in riparian wetlands (Dupas et al., 2015b, 2016).

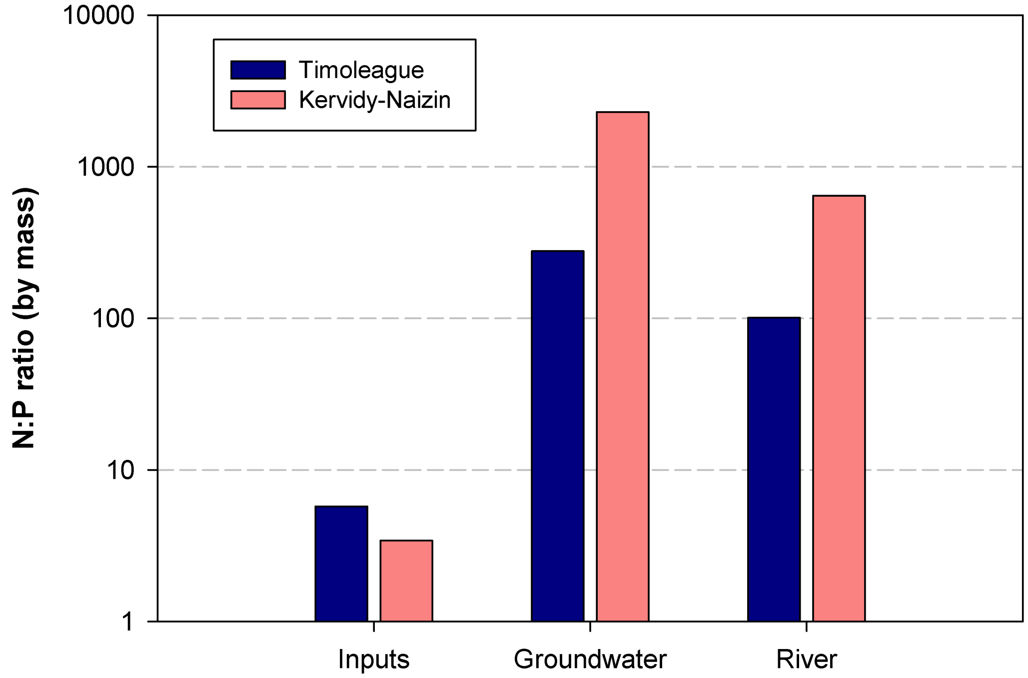


Figure 7: N:P ratios along the nutrient transfer continuum. “Inputs” were calculated from chemical and organic N and P fertiliser application. “Groundwater” was calculated from mean nitrate-N and soluble P groundwater concentration. “River” was calculated from nitrate-N and soluble P river loads (October 2010 – September 2015).

3.3. Comparison of factors controlling N and P leaching

Table 2 summarises the soil-climate-land use factors that were compared in this study to explain the different amounts of nitrate-N and soluble P leaching in Kervidy-Naizin and Timoleague. All factors (except source factors) that are known to increase nitrate-N leaching were higher in the Kervidy-Naizin catchment and all factors (except source factors) that are known to increase soluble P leaching were higher in the Timoleague catchment, and this is reflected in the catchment outputs respectively.

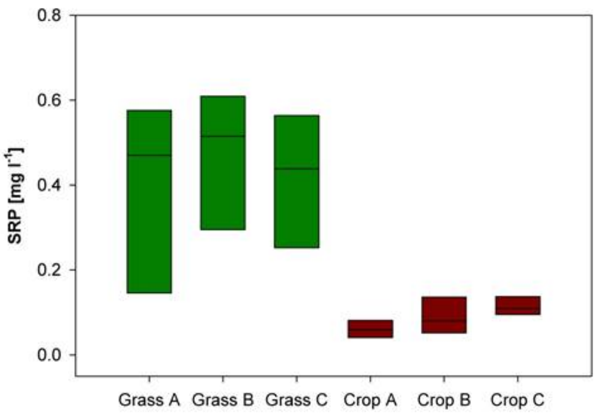
In temperate climates the autumn-winter conditions are critical in determining nitrate-N leaching because of the risk of a temporal mismatch between the presence of high concentrations in the soil and plant uptake capacity (Moreau et al., 2012) combined with high drainage potential. The soil organic N represents an important N storage pool (Sebilo et al., 2013) which can subsequently release nitrate-N through mineralisation, especially when the soil C:N ratio is low. Although the soil C:N ratio was similar in the two catchments, higher autumn temperature in Kervidy-Naizin may lead to higher mineralisation rates than in Timoleague (Rodrigo et al., 1997; Table 2). The main crops in the Kervidy-Naizin catchment, winter cereals and maize, do not take up N efficiently in the autumn – winter period (Dupas et al., 2015d). Furthermore, grasslands in the Timoleague catchment have a seemingly better capacity to take up N from the soil throughout the year, particularly in the autumn – winter period (McDowell et al., 2014) and reduce N leaching compared to cropland (Moreau et al., 2012; Rode et al., 2009), although urine patches in grazed grassland can be hotspots of nitrate leaching..

The abundance of Al oxide is an indicator of a soil's adsorption capacity with P (Daly et al., 2015; Schoumans and Chardon, 2015). Extractable Al in the Kervidy-Naizin catchment (using oxalate extraction) was 3.4 times higher than in Timoleague (using Mehlich 3 extraction), while previous studies have shown that the difference in extraction rates between the two methods was less than 2 (Sims et al., 2002; Zhang et al., 2005). Hence the maximum P sorption capacity of soils in the Kervidy-Naizin catchment was probably higher than that of soils in the Timoleague catchment. The abundance of Fe oxide has also been used as an indicator of a soil's adsorption capacity (e.g. Schoumans and Chardon, 2015) but it can also favour the formation of colloidal Fe-P forms, which can increase leaching (Daly et al., 2015; Mellander et al., 2016; Pautler and Sims, 2000). Extractable Fe in the Kervidy-Naizin catchment (using oxalate extraction) was 10.5 times higher than in Timoleague (using Mehlich 3 extraction), while previous studies have shown that the difference in extraction rates between the two methods varied between ca. 5 - 12 (Sims et al., 2002; Zhang et al., 2005). Hence the influence of Fe oxides in soils on P leaching between the two catchments is ambiguous and it is difficult to conclude which catchment has the highest abundance of extractable iron due to different extraction methods. The abundance of high organic matter content in soils may increase P leaching by competing with P adsorption sites (Kang et al., 2009) and favour the formation of easily leachable organic colloids (Granger et al., 2007). These may be destabilised as rainwater with a lower ionic strength than the soil water reaches the subsoil (Ilg et al., 2005). Organic matter content in the Timoleague catchment was 74% higher than in Kervidy-Naizin. Therefore, with the soil data available, Timoleague exhibited a higher risk of P leaching regarding all the soil characteristics available for this comparative study. Subsoil properties have also been found to be critical for P leaching, and particularly in sandy soils with high P sources, high degrees of P saturation and low sorption capacities (Andersson et al., 2015). The subsoils have not been investigated in this study but may have a role in the higher P leaching in Timoleague.

The dominance of grassland in the Timoleague catchment could also increase the risk of P leaching compared to the mainly arable Kervidy-Naizin catchment. Presence of grassland increases organic matter content, which was previously identified as increasing the risk of P leaching (Djodjic et al., 2004; Gachter et al., 1998; Haygarth et al., 1998). In particular, a review by Darch et al. (2014) has highlighted the potentially high contribution of soluble organic P to total soluble P leaching in temperate agricultural soils (up to 80%), especially when a rainfall occurs after slurry application. Although soluble organic P was not considered in the current study, it may have contributed to the SRP measured in the groundwater and the stream (after hydrolysis). Grassland may also favour the formation of macropores, which increases the risk of preferential flow, because grassland is not frequently disturbed by tillage thus biologically formed macropores (such as by roots or earthworms) are preserved (Simard et al., 2000). Furthermore, root exudates from grassland may stimulate the activity of soil microbes increasing P solubilisation (Roberts et al., 2013; Stutter et al., 2009) and drying-rewetting cycles may release soluble organic and inorganic P from the microbial biomass (Blackwell et al., 2010; Dupas et al., 2015c; Gu et al., 2017).

Because soil, climate and land use factors covary in the two catchments studied, Kervidy-Naizin data from mini-piezometers placed in two adjacent plots with contrasting land uses but similar soil chemistry and climate (Fig. 8) help to interpret the specific effect of land use on P solubilisation. The two plots exhibited similar soil P content and extractable Al and Fe and sampling points were at similar positions along the hillslope. However, organic matter content in the grassland plot was 87% higher than in the arable cropland plot. Results showed that P solubilisation was 4.7 times higher in the grassland plot compared to the cropland plot (Mann-Whitney test, $p < 0.05$; Fig. 8), either because of a direct effect of the plant type or via an increase in organic matter content. In the Timoleague catchment, where inputs of organic P are applied during grazing and spreading, leaching of soluble P is possibly even higher (Darch et al., 2014).

[Please insert Table 2 here]



	Grass (buffer strip)	Crop
P Dyer [mg kg^{-1}]	288.5	362.6
Al [mg kg^{-1}]	1690	1100
Fe [mg kg^{-1}]	4250	4450
OM [%]	7.1	3.8

Figure 8: Soluble Reactive Phosphorus (SRP) concentration in the soil solution sampled from two adjacent plots (grass and crop) at 4-5 cm (mini-piezometers in triplicate: A, B, C) in the Kervidy-Naizin catchment. Box-plots represent the median and 10th-90th percentile of five sampling dates during the 2013-2014 water year for each replicate. The table provides the mean value for each plot of soil Dyer P, aluminium, iron and organic matter contents.

3.4. <u>Catchment trajectories</u>

The catchment monitoring programmes both in Western France and South-western Ireland aim to provide underpinning knowledge on N and P transfer processes to support sustainable agricultural practices in a context of adaptive management, climate and land use changes. In Western France, research and management efforts to reduce nutrient pollution have long been directed towards N rather than P. This is because Western France is a coastal region where the risk of green algae development in several bays (where N is deemed to be the limiting nutrient) is the main concern for policy makers (Levain et al., 2015). Conversion of cropland to grassland has been identified previously as an efficient way of reducing nitrate-N leaching while maintaining good economic performance (Moreau et al., 2012). The present comparative study with a grassland catchment in South-western Ireland tends to confirm the beneficial role of grassland in decreasing nitrate-N losses. However, this comparison also raises the question of a risk of pollution swapping, with a possible increase of P mobilisation if arable land is converted into (intensive) grassland. In this regard, the influence of organic matter on Al/Fe complexes will be important to determine. The ambivalent role of (intensive) grassland in controlling N and P mobilisation has recently been highlighted at the field and farm scale in the United-Kingdom (Peukert et al., 2014). In a scenario where P mobilisation and transfer increase because of management measures that only target nitrate-N mitigation and reduction of coastal green tides, eutrophication of adjacent freshwaters is a possibility.

The Timoleague catchment also drains into estuarine waters with both N and P deemed to be limiting nutrients in the Irish context (Longphuirt et al., 2015). Studies in this catchment have highlighted how reductions in mean flow-weighted P concentrations have occurred in the quickest (i.e. shallowest) flow pathways due to reduced P source pressures, while maintaining milk production yields at the highest level (Murphy et al., 2015). While this indicates an increased catchment resilience, most likely related to reductions in the highest soil P concentrations and conforming to regulations on nutrient management (Wall et al., 2011), care is required on the trajectory of changes that might be observed under future land use changes. For example, scenarios to increase milk production under grassland and also under existing regulations may require grasslands to increase grass yield.

The potential risk of increasing nutrient losses under land use change or intensification may be exacerbated by climate change in both Western France and South-western Ireland. With increasing mean annual temperature, and particularly autumn temperature, N mineralisation is expected to increase (Rodrigo et al., 1997) causing higher nitrate-N leaching if plant uptake rates and timing are not adequately adapted. Concerning soluble P, the increasing occurrence of wetter periods following drier periods (Ockenden et al., 2016) is also expected to increase solubilisation (Blackwell et al., 2010; Dupas et al., 2015c; 2016) and potentially leaching.

4. Conclusion

In two groundwater-driven and intensively farmed catchments on the Atlantic seaboard of Europe (Western France and Southwest Ireland), mobilisation processes appeared to play a dominant role in the contrasting export of nitrate-N and soluble P from land to the receiving streams. Nitrate-N leaching was mainly controlled by mineralisation and the timing of plant uptake: grasslands have a longer growth period and better utilisation of N than cropland, hence grasslands reduced nitrate-N leaching. Soluble P leaching was mainly controlled by the soil adsorption capacity and land use, with an increased P solubilisation in grassland compared to arable cropland. Near-stream attenuation of nitrate-N, likely through denitrification and dilution, and enrichment in soluble P, through soil-groundwater interactions, were similar in both catchments. This study highlighted the potential risk of pollution swapping between dominant nitrate-N transfer and dominant soluble P transfer in a context of land use change in groundwater fed catchments. Further research will be required to better quantify the risk of increased nitrate-N and soluble P transfer when switching from arable land to grassland, or the other way around, and to take account of interactions with soil chemistry and climate in similar catchments.

Acknowledgement

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