



# Anthropogenic feed and food trade and hydrological factors influence river N and P export and stoichiometry from heavily exploited watersheds

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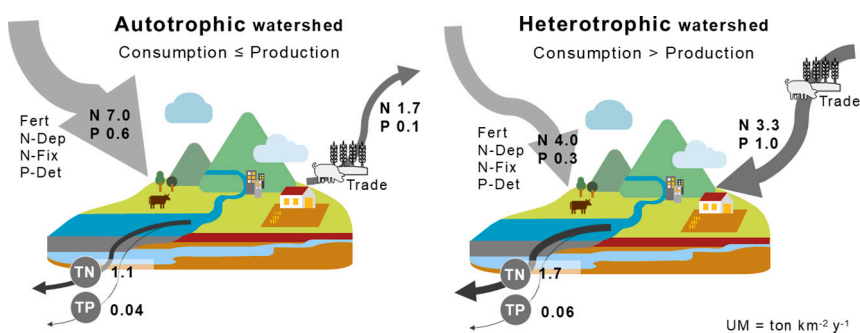
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## HIGHLIGHTS

- Anthropogenic nitrogen and phosphorus inputs (NANI/NAPI) highly variable across human impacted watersheds
- Nutrient trade balance defines watershed autotrophy or heterotrophy.
- Exported nutrient loads depend on input magnitude and trophic status of watersheds.
- Hydrology modulates how trophic status affects nutrient export variability.
- The NANI:NAPI input ratio differs by trophic status and from the TN:TP output ratio.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Over the last century, agricultural intensification and urban expansion have significantly disrupted nitrogen (N) and phosphorus (P) cycles, with detrimental effects on the integrity of aquatic ecosystems. Nonetheless, current understanding of riverine nutrient dynamics – naturally influenced by geo-hydrological and climatic features – is still incomplete. This study aims to understand how the composition of the anthropogenic nitrogen and phosphorus load and geo-hydrological watershed characteristics influence riverine loads. To investigate these aspects, a trophic classification was applied to distinguish autotrophic (production-driven) watersheds typically associated with fertilizer use from heterotrophic (consumption-driven) systems, which rely on imported feed and food. Our analysis focused on the Po River Hydrographic District, one of the regions most impacted by N and P contamination in Europe. Net Anthropogenic Nitrogen and Phosphorus Inputs (NANI and NAPI), riverine N and P exports, and geo-hydrological characteristics were assessed to understand export variability between trophic groups. In autotrophic systems, nitrogen export was more influenced by hydrology than by NANI levels. Conversely, nitrogen loads were closely associated with manure and feed imports in heterotrophic watersheds,

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with runoff and leaching acting as primary pathways. Phosphorus export was largely governed by erosion and soil retention, showing a weak correlation with NAPI. Although N:P input ratios differed between groups, output ratios tended to converge, suggesting that different processes regulate nutrient stoichiometry.

## 1. Introduction

Expansion of agricultural land, intensive livestock farming, and urbanization have altered about three-quarters of the Earth's ice-free surface, reducing the capacity of ecosystems to absorb and metabolize nutrient inputs (Ellis et al., 2010; Pinay et al., 2015; Seitzinger et al., 2010). In particular, land colonization and human metabolism have radically transformed the transport and processes of nitrogen (N) and phosphorus (P) within and across watersheds (Conley et al., 2009; Smith, 2016; Sutton et al., 2013). In addition, in the second half of the twentieth century, global fertilizer use has increased by more than 500 %, while the production and trade of N and P in the form of animal and plant proteins have increased eightfold, leading to a significant N and P exchange between watersheds (Foley et al., 2011; Lassaletta et al., 2014b). As a result, excess nutrients continue contaminating surface and groundwater, increasing transfer through the hydrological system, and altering nutrient stoichiometry, with the resulting eutrophication being considered one of the greatest contemporary threats to many lakes, estuaries, and coastal areas worldwide (Glibert, 2017; Le Moal et al., 2019; Wurtsbaugh et al., 2019). Control, buffering, and remediation of eutrophication have been intermittently successful, partly due to the increasing relevance (if not dominance) of diffuse N and P sources, which challenge our ability to identify and control the factors influencing nutrient load generation (Le Moal et al., 2019).

Human activities are the primary source of nutrient excess in anthropized watersheds, and various approaches - ranging from mechanistic modelling description of nitrogen transfer and transformation processes to statistical regression analyses - have been developed to relate watershed nutrient inputs to outputs in downstream and coastal marine ecosystems and identify the responsible drivers and processes (Schoumans et al., 2009; Shan et al., 2023; Swaney et al., 2012). Among these, mass balances like the Net Anthropogenic Nitrogen and Phosphorus Inputs (NANI and NAPI) are widely used and have shown a variable relationship between NANI, NAPI, and riverine N and P export dynamics (Goyette et al., 2016; Hong et al., 2017; Howarth et al., 1996; Viaroli et al., 2018). On average, 20 % of the net N and 5 % of the net P inputs are exported from watersheds, but the relative export fractions vary between 5 and 50 % and 1 and 15 %, respectively. This variability is due to the interaction among several factors, including urbanization, the organization of the agricultural system, the geological and hydrological characteristics of the watershed, and the biogeochemical characteristics of the elements that affect mobilization and retention across land and waterscapes (Goyette et al., 2019; Lassaletta et al., 2012; Romero et al., 2021; Shousha et al., 2023).

The organization of the agricultural system (i.e. amount and type of crop production and livestock farming) can affect load variability by influencing the magnitude and the form of the net input of both N and P. Concerning this, Billen et al. (2010) introduced the concept of anthropogenic autotrophy and heterotrophy of watersheds to summarize information about the organization of agricultural activities in a territory. Specifically, watersheds that exhibit a net export of nitrogen in the form of feed and/or food, are classified as autotrophic, whereas those that exhibit a net import are classified as heterotrophic. Therefore, in many net autotrophic watersheds, synthetic fertilizers are the single largest input to agricultural fields and contribute to diffuse sources. On the other hand, net heterotrophy is a proxy for sewage and animal manure excesses, ultimately derived from imported food and feed that support large urban populations or intensive livestock production (Billen et al., 2010). Importantly, loads exported from diffuse sources are strongly linked to precipitation patterns (Lassaletta et al., 2012; Romero et al.,

2021), while point sources (e.g., wastewater treatment plants) generate a more constant load over time, which appears to be less dependent on hydrogeological conditions (Abbott et al., 2018; Musolf et al., 2015). Urbanization also contributes to modifying exports: land sealing alters the intensity of floods and the hydrological regime (O'Driscoll et al., 2010) and simplification of river networks decreases the retention capacity and the buffering effect of riparian environments (Mason et al., 2025; Newcomer Johnson et al., 2016). Concurrently, river damming affects export times and modifies the composition of the N and P pools (Maavara et al., 2020). Moreover, the biogeochemical characteristics of the elements influence their mobility, with different effects on N and P transport (Cavallini et al., 2024). Given the high nitrate ( $\text{NO}_3^-$ ) solubility, N is more easily leached and transported by surface and subsurface runoff (Dupas et al., 2016; Howarth et al., 2012) while P is more reactive and less mobile, easily adsorbed by soil particles, and is mainly exported from uncovered soils by the erosive action of rain (Baker et al., 2015; Kalkhoff et al., 2016).

Given this complexity, the weight of different factors and how their role varies in combination with physical and hydrological characteristics remains uncertain, although understanding the drivers of N and P fluxes in watersheds has been a major focus of research over the past four decades (Goyette et al., 2016; Howarth et al., 1996; Shousha et al., 2023). Furthermore, whereas the dynamics of N have been extensively studied, the contribution of the different factors in regulating the stoichiometric N:P ratio is poorly understood.

This study aims to understand if the trophic status of watersheds, defined as anthropogenic nitrogen autotrophy and heterotrophy according to Billen et al. (2010), can be used as an index to better predict the magnitude and composition of river nutrients export. This classification, originally based only on the net input of N trade, synthetically describes the dominant processes (production vs. consumption) and implicitly considers variations in N export mechanisms and their interactions with the hydrological system. In this research, we extend this concept also to P to examine how different types of anthropogenic inputs affect both N and P cycling within the Po River Hydrographic District (PRHD), one of the areas with the greatest impact due to human activity in Europe (Viaroli et al., 2018). Our study hypothesizes that the imbalance between production and consumption affects both the export magnitude and the pool composition of exported total nitrogen (TN) and total phosphorus (TP). The three specific goals of our study are: (i) analyze the influence of hydrological processes on nutrient export and its variability between trophic groups; (ii) investigate how the interaction between trophic status and hydrology modulates export efficiency and (iii) unveil how these factors together shape deviations from the input N:P ratio (NANI:NAPI), potentially revealing key regulatory points in the nutrient dynamics.

Specifically, we examined in which way trophic status and geo-hydrological features influence the relationship between anthropogenic inputs (NANI and NAPI) and the exported loads of various forms of nitrogen and phosphorus, as well as their stoichiometric ratios. We examined the same relationship, which includes anthropogenic inputs of nitrogen and phosphorus along with geohydrological variables, at the watershed scale according to their trophic status.

Within the PRHD, the sub-basins spanned gradients of human pressure and natural environments, inputs from fertilizer, food, and feed imports, and climatological and hydrological variability, providing an opportunity to investigate the drivers that influence N and P export.

## 2. Materials and methods

### 2.1. Study area

This study was conducted in 42 river watersheds located within the PRHD (Northern Italy), a water management area defined under the Water Framework Directive (Legislative Decree 152/2006; <https://www.gazzettaufficiale.it/dettaglio/codici/materiaAmbientale>) (Fig. 1A). The PRHD has a total surface area of 86,800 km<sup>2</sup>, of which 85 % (74,000 km<sup>2</sup>) belongs to the Po River catchment - the main river draining into the Adriatic Sea and one of the largest rivers in southern Europe. Our study area encompasses approximately 72,300 km<sup>2</sup> and includes both the tributary watersheds of the Po River, which cover 84 % of Po basin at Pontelagoscuro closing station, and those rivers within the PRHD that drain directly into the Adriatic Sea (Fig. 1B). Of the 42 watersheds analyzed, 35 flow directly into the Po River and drain 88 % of its total catchment area, while the remaining 7 flow directly into the Adriatic Sea (Fig. S1 in Supplementary material). Within the selected watersheds, land cover is approximately 47 % anthropized, consisting primarily of agricultural areas (40 %) and artificial surfaces (e.g. urban fabric, transportation infrastructure, green urban areas) (7 %). The remaining area (53 %) is classified as natural land cover, comprising forests (31 %) and semi-natural (20 %) areas and water bodies (2 %), according to the Corine Land Cover database (2018). The average population density is 232 ind. km<sup>-2</sup>, while livestock units (1 LU = 1 adult dairy cow) account for 48 LU km<sup>-2</sup>. The spatial distribution of land use is heterogeneous, with agricultural areas concentrated in lowlands, where anthropogenic activity has developed a dense and capillary artificial hydrographic network, deeply interconnected and difficult to separate from the natural framework (Soana et al., 2023) (Fig. 1). The territory comprises eight different Hydro-ecoregions: Inner Alps East, Inner Alps Central, Inner Alps South, Southern Pre-Alps and Dolomites, Apennines North, Piedmont Apennines, Monferrato, Po Plain (Wasson et al., 2007). The Alpine (North) and Apennine (South) sides of the district have different hydrological characteristics. The Alpine side is

characterized by the presence of a great number of both high-altitude small lakes and reservoirs, and five large deep subalpine lakes fed by Alpine glaciers (Lakes Maggiore, Como, Iseo, Idro and Garda), while lakes located on the Apennine side lack significant water storage. As a result, the south side of the watershed is affected by water scarcity, and streams and rivers have an extremely variable flow regime. The 42 watersheds included in this study encompass different climatological and physical characteristics, and the surface area of the watersheds varies between 106 and 8260 km<sup>2</sup> (Fig. 2, Table S1 in Supplementary materials).

The investigated watersheds were selected according to the following criteria: (i) the catchment areas are independent; (ii) the sampling stations for concentration and discharge measurements are spatially coupled or as closest as possible and located in a closing section that drains more than 80 % of the total catchment area (Fig. S2, Supplementary materials); (iii) the concentration sampling data are homogeneously distributed over the considered years (Table S3, Supplementary materials); (iv) the flow data are available with daily frequency for more than 80 % of the entire period. Data used in this study to calculate nutrient input, output and riverine loads were obtained from several water authorities and statistical institutions, as described in the following sections.

### 2.2. Net anthropogenic nitrogen and phosphorus input to watersheds

Net anthropogenic N and P inputs were calculated using the Net Anthropogenic Nitrogen Input (NANI) and the Net Anthropogenic Phosphorus Input (NAPI) approaches, respectively. The NANI methodological approach was initially introduced by Howarth et al. (1996), and then adapted and applied also to quantify the net anthropogenic P input (Han et al., 2013; Hong et al., 2012; Russell et al., 2008). NANI (kg N km<sup>-2</sup> y<sup>-1</sup>) and NAPI (kg P km<sup>-2</sup> y<sup>-1</sup>) were quantified as follows:

$$NANI = N_{DEP} + N_{FERT} + N_{FIX} + N_{FEED} + N_{FOOD} \quad (1)$$

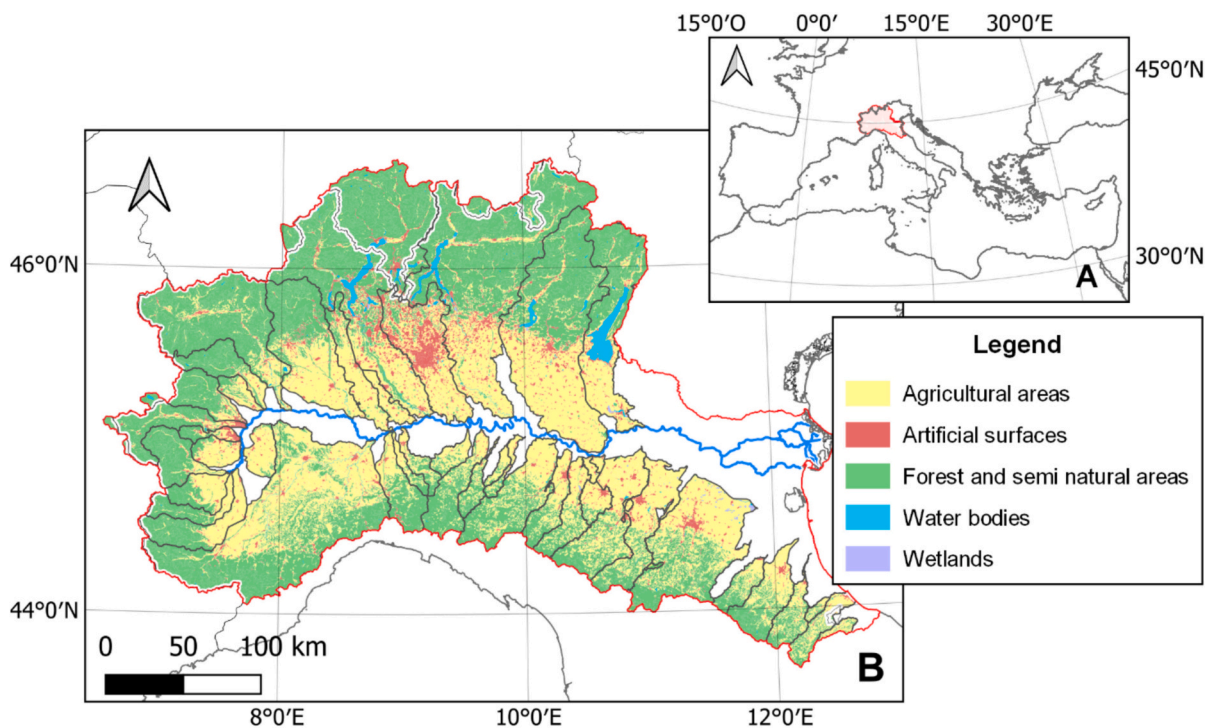
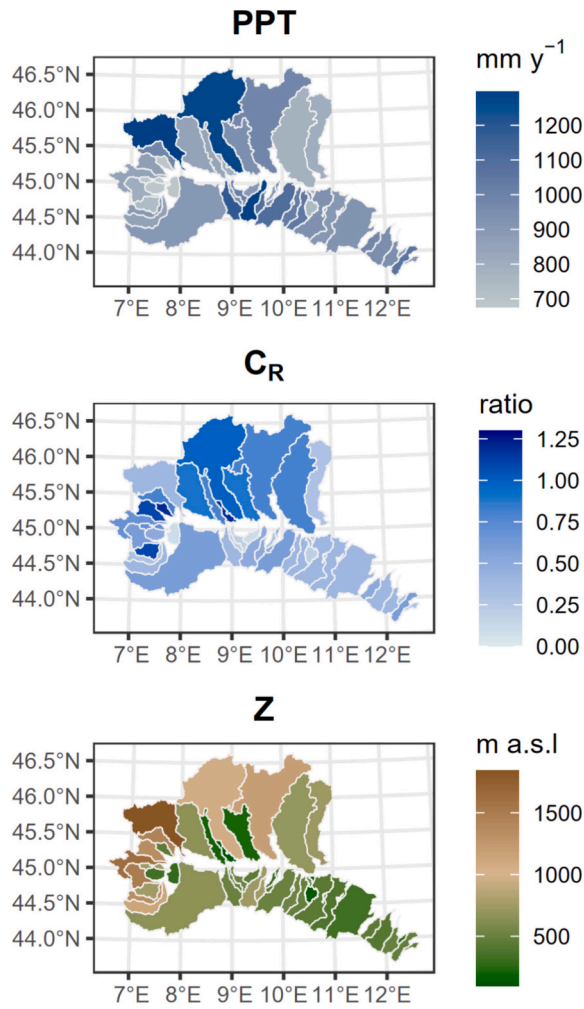


Fig. 1. (A) Po River District within the broader context of the Mediterranean area. Additional maps with watersheds names (S1) and station positions (S2) are shown in Supplementary materials. (B) shows soil use (Corine Land Cover, 2018 - <https://land.copernicus.eu/en/products/corine-land-cover/clc2018>), of the investigated watersheds within the Po River District (red solid line), with the national border (white-black solid line) and the main course of Po River (blue solid line).



**Fig. 2.** Geo-hydrological characteristics of the catchment areas of the Po River watershed: runoff coefficient ( $C_R$ ), total precipitation (PPT), and average altitude ( $Z$ ). For the average altitude color change point is equal to 1000 m a.s.l.

$$NAPI = P_{FERT} + P_{DET} + P_{FEED} + P_{FOOD} \quad (2)$$

where  $N_{DEP}$  = atmospheric N deposition on the total watershed area;  $N_{FERT}$  and  $P_{FERT}$  = synthetic N and P fertilizer applied to agricultural land;  $N_{FIX}$  = agricultural  $N_2$  fixation associated with N-fixing crops;  $P_{DET}$  = non-food use of P by human (detergents);  $N_{FEED}$  and  $P_{FEED}$  = net exchange of N and P as feed trade;  $N_{FOOD}$  and  $P_{FOOD}$  = net exchange of N and P as food trade. Trade components can assume both positive (net import of N or P with commercial feed or food exchanges) or negative values (net export of N or P with commercial feed or food exchanges). NANI and NAPI are presented as normalized for the watersheds area. A more detailed description of NANI and NAPI calculation and data sources is available in the Supplementary materials.

### 2.3. Hydrological and geospatial characteristics of the watersheds

Total precipitation (PPT) data were extracted from E-OBS raster files provided by the Copernicus Climate Change Service (<https://surfobs.climate.copernicus.eu/>) with a grid resolution of  $0.1^\circ$  (Cornés et al., 2018). The precipitation data represents the sum of the amount of rain, snow, and hail measured as the height of the equivalent liquid water in a square meter and were calculated as the sum of the mean daily precipitation per watershed in a year.

The average elevation ( $Z$ ) of each watershed was calculated from DEM files of the Geographic Information System of the Commission

(GISCO) (<https://ec.europa.eu/eurostat/web/gisco>) provided by the Copernicus service with a resolution of  $2.5^\circ$  using the *sf* R package (Pebesma and Bivand, 2023).

The runoff coefficient ( $C_R$ ) was estimated on an annual basis as the ratio between areal runoff, calculated as the sum of daily discharge values, and precipitation (PPT). For statistical analyses, we employed the mean  $C_R$  calculated only for the years in which nutrient load estimation was feasible within the period of this study (2014–2019).  $C_R$  is the inverse of hydraulic retention capacity and an indicator of hydrological balance of a watershed. It can also be interpreted as a proxy of hydrological connectivity, since water infiltration, evapotranspiration or human demand contribute to stream intermittency (McDonnell et al., 2021; Sarremejane et al., 2022).

### 2.4. Riverine N and P loads estimation

The average annual riverine nutrient loads exported from the watersheds were calculated over the period 2014–2019 for the following forms: total nitrogen (TN), nitrate ( $N-NO_3^-$ ), ammonium ( $N-NH_4^+$ ), total phosphorus (TP), and soluble reactive phosphorus (SRP). The period was selected to calculate the exported load within a time frame comparable to that used for NANI and NAPI quantification and to average years with different hydrological characteristics.

The annual load was calculated as the product of the discharge-weighted mean concentration and the mean annual discharge (Quilbé et al., 2006) as follows:

$$L = \frac{\sum_{i=1}^n C_i * Q_i}{\sum_{i=1}^n Q_i} * \bar{Q} * k \quad (3)$$

where:

$L$  = annual loading ( $kg\ y^{-1}$ )

$C_i$  = instantaneous concentration measured at day $_i$  ( $g\ m^{-3}$ )

$Q_i$  = mean daily discharge for day $_i$  ( $m^3\ s^{-1}$ )

$\bar{Q}$  = mean annual discharge ( $m^3\ s^{-1}$ )

$k$  = conversion factor from  $g\ s^{-1}$  to  $kg\ y^{-1}$ .

The average annual load was then calculated as the average of annual loads estimated for the years analyzed. Finally, the loads were normalized by dividing for the watershed area.

Nutrient concentration data were gathered from institutional monitoring campaigns conducted by the Regional Environmental Protection Agencies (ARPA) of the Po River District for the assessment of ecological status in accordance with the Water Framework Directive. Sample collection and analysis were performed by standard methods and analytical protocols adopted by ARPA (IRSA-CNR and A. P. A. T., 2003). Sampling frequency varied from once a month to once a season, with a general mean of nine sampling per year (Table S3), following ARPA monitoring protocol which is defined by the Italian Law D.M. 260/10 (<https://www.gazzettaufficiale.it/eli/id/2011/02/07/011G0035/sg>). Data were downloaded from the following online repositories: <https://dati.arpae.it/dataset> (Emilia-Romagna), <http://webgis.arpae.piemonte.it/geoportale> (Piedmont) and <https://www.dati.lombardia.it> (Lombardy).

Flow data are publicly available on a daily scale and were downloaded from the following repositories: Emilia-Romagna (<https://simc.arpae.it/dext3r/>), Piedmont ([https://www.arpae.piemonte.it/rischi\\_naturali/snippets\\_arpae\\_graphs/map\\_meteoweb/?rete=stazione\\_meteorologica](https://www.arpae.piemonte.it/rischi_naturali/snippets_arpae_graphs/map_meteoweb/?rete=stazione_meteorologica)) and Lombardy (<https://idro.arpalombardia.it/it/map/sidro/>). In the case of incomplete discharge datasets, the issue was addressed differently depending on the length of the period with missing data. Flow data unavailable for periods of less than two days were recalculated by linear interpolation. For gaps of more than two days and less

than one month, data from the nearest station was used. If data were missing for longer periods, or if the estimate from the nearest station was not considered reliable, the entire year was excluded, resulting in the elimination of eleven out of 252 calculated years.

### 2.5. Statistical approach and analysis

The dataset was grouped according to the trophic state of the watersheds to determine if the composition of anthropogenic inputs affects the exported load. According to Billen et al. (2010), watersheds with negative trade values are autotrophic, while those with positive trade values are heterotrophic. Our watersheds were not evenly distributed between these categories, and separate classifications based on N-trade and P-trade led to unbalanced groupings, with 30 heterotrophic watersheds for N and 35 for P. To address this issue, we classified watersheds with positive trade for both N and P as clearly heterotrophic, while those with negative or null trade were categorized as autotrophic. This approach resulted in a classification of 30 heterotrophic watersheds and 12 autotrophic or “at equilibrium” watersheds.

First, to analyze the effect of grouping according to the trophic state, we used the Kruskal-Wallis test to examine differences within NANI, NAPI, their components, and exported loads. The average values for the three groups (general for all the watersheds, heterotrophic, and autotrophic) were presented as area-weighted averages, and correlation analysis between NANI and NAPI components were carried out by applying the Kendall test. Only  $\tau$  values greater than 0.4 were taken as relevant.

Second, the relationships between exported loads, anthropogenic inputs, and hydrological and geospatial characteristics were estimated using linear regression.

As exploration analysis, we examined only the individual relationships between total anthropogenic inputs and exported loads, specifically: NANI vs. TN, NAPI vs. TP, and the NANI: NAPI ratio vs. the TN: TP molar ratio.

Then, we conducted multiple linear regressions for each form of nitrogen and phosphorus, as well as for their stoichiometric ratios, incorporating NANI or NAPI and PPT,  $C_R$ , and Z. The formulas used were as follows:

$$N \sim NANI + PPT + C_R + Z \quad (4)$$

$$P \sim NAPI + PPT + C_R + Z \quad (5)$$

$$\frac{N}{P} \sim \frac{NANI}{NAPI} + PPT + C_R + Z \quad (6)$$

where:

N is alternatively the exported load of TN,  $N-NO_3^-$  or  $N-NH_4^+$  ( $kg\ km^{-2}\ y^{-1}$ ).

P is alternatively the exported load of TP or SRP ( $kg\ km^{-2}\ y^{-1}$ ).

N:P is alternatively the molar ratio of TN: TP or DIN: SRP.

$C_R$  is the Runoff coefficient (ratio).

PPT is the total cumulated precipitation ( $mm\ y^{-1}$ ).

Z is the mean altitude (m a.s.l.).

Finally, we applied the previous multiple linear regression (MLR) models (formulas (4) to (6)) separately for autotrophic and heterotrophic watersheds. As the autotrophic group had fewer observations, we chose to repeat the analysis by considering only anthropogenic inputs and one geohydrological variable at a time. We then reported the best-performing model among the three tested.

To address potential collinearity among variables, before carrying out the statistics of the MLR models we applied the Variance Inflation Factor (VIF), using a  $VIF \geq 5$  as a reference point, as suggested by Graham (2003) and Mason et al. (2003). For all models, the included variables were normalized for area and log-transformed to reduce

skewness, and finally scaled to avoid bias due to different units or dimensionlessness.

Data processing was carried out with R (R Core Team, 2022) and model information was analyzed using *parameters* (Lüdecke et al., 2020) package. Model validation was performed by analyzing the assumptions via the graphical output of the residuals as described in Zuur et al. (2009).

## 3. Results

### 3.1. Physical features of the watersheds

The 42 watersheds are characterized by a high degree of hydrogeological diversity (Fig. 2). The average PPT is  $908\ mm\ y^{-1}$  (min = 676, max = 1.297) and the run-off is  $479\ mm\ y^{-1}$  (min = 60, max = 1.214). Precipitation and runoff are spatially independent, confirming the hydrological heterogeneity of the district and the presence of different factors that may influence the hydrological balance, while  $C_R$  varies from 0.1 to 1.2 (average = 0.55).

The average watershed altitude varies between 97 and 1841 m a.s.l. (mean value 497 m a.s.l.), the average slope varies between  $0.8^\circ$  and  $27^\circ$  (mean =  $14.4^\circ$ ), and the mean temperature is  $12.6\ ^\circ C$  (min =  $4.8\ ^\circ C$ , max =  $14.3\ ^\circ C$ ). Due to the high correlation between these three variables ( $r_{z-m} = 0.9$ ,  $p < 0.01$ ;  $r_{z-T} = -0.95$ ,  $p < 0.01$ ), it was decided to keep only the mean altitude in the MLR.

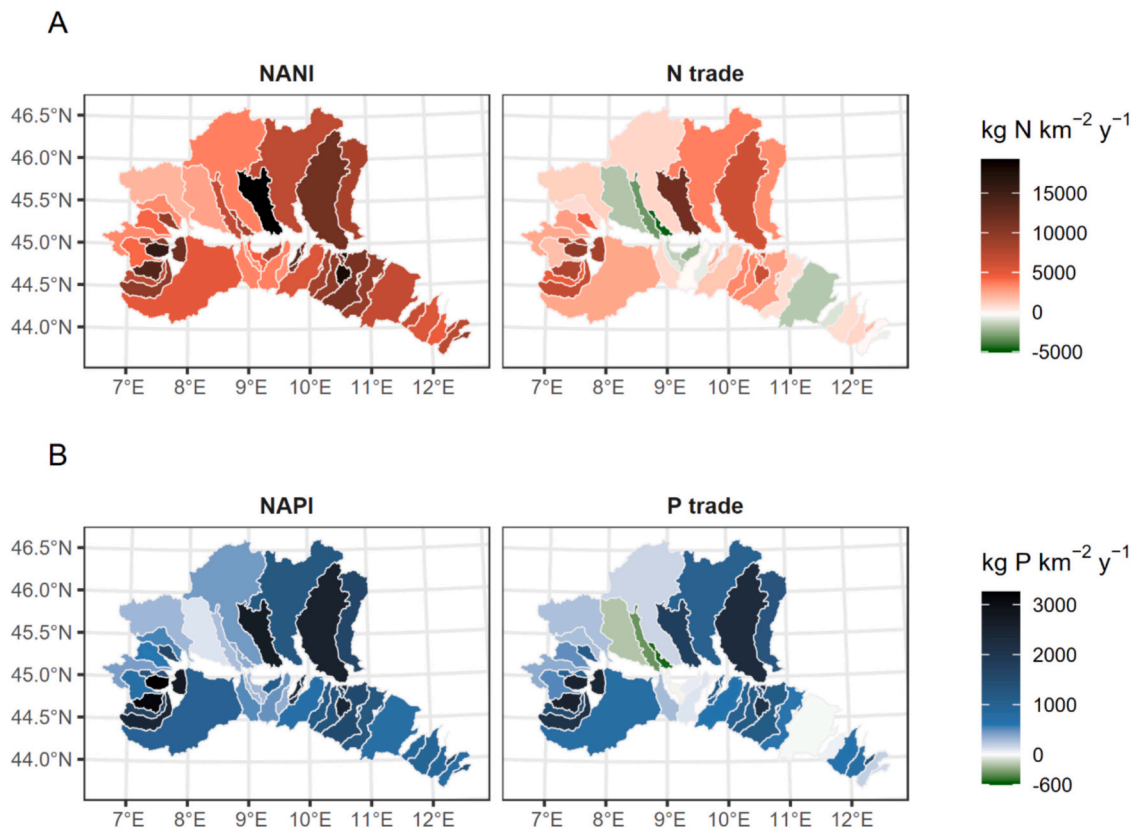
### 3.2. Net anthropogenic N and P inputs to watersheds

The average net anthropogenic N and P inputs were  $7074\ kg\ N\ km^{-2}\ y^{-1}$  (ranging from 2039 to  $19,258\ kg\ N\ km^{-2}\ y^{-1}$ ), and  $1157\ kg\ P\ km^{-2}\ y^{-1}$  (ranging from 114 to  $3257\ kg\ P\ km^{-2}\ y^{-1}$ ) respectively (Fig. 3). Overall, the area investigated is net heterotrophic with net feed and food import, both for N ( $2,480\ kg\ N\ km^{-2}\ y^{-1}$ ) and P ( $823\ kg\ P\ km^{-2}\ y^{-1}$ ). However, absolute net N and P inputs, and their components show a high spatial variability among the catchments and specifically considering the trophic state grouping.

NANI ranges from an average of  $5336\ kg\ N\ km^{-2}\ y^{-1}$  in the autotrophic group to an average of  $7320\ kg\ N\ km^{-2}\ y^{-1}$  in the heterotrophic group ( $p < 0.05$ ) (Fig. 4 left). In the heterotrophic watersheds (Fig. 5), NANI is primarily associated with fertilization and trade ( $\tau = 0.53$ ), with feed trade ( $3090\ kg\ N\ km^{-2}\ y^{-1}$ ) and fertilization ( $1992\ kg\ N\ km^{-2}\ y^{-1}$ ) representing the main N inputs. Notably, net trade is more strongly linked to feed ( $\tau = 0.60$ ) than to food, while fertilization is not correlated with the other inputs (Fig. 5). Fertilization is higher in the autotrophic group where it dominates the N inputs ( $\tau = 0.55$ ), compared to the heterotrophic ( $4555\ vs\ 1992\ kg\ N\ km^{-2}\ y^{-1}$ ,  $p < 0.05$ ). Net negative trade reduces NANI with respect to heterotrophic watersheds, and it is positively correlated with fertilization and food, while a negative correlation ( $\tau = -0.48$ ) between feed export and N fixation was detected (Fig. 5).

Nitrogen fixation, ranging from 281 to  $8398\ kg\ N\ km^{-2}\ y^{-1}$ , does not show statistically significant differences between the autotrophic and heterotrophic watersheds and represents 21 % of NANI at the district scale. Finally, although atmospheric deposition does not vary in absolute terms between the groups (ranging from 306 to  $1359\ kg\ N\ km^{-2}\ y^{-1}$ ), its contribution to NANI is higher in heterotrophic than in autotrophic watersheds (13.3 % vs 8.8 %,  $p < 0.05$ ).

NAPI halves when moving from heterotrophic ( $1257\ kg\ P\ km^{-2}\ y^{-1}$ ) to autotrophic watersheds ( $506\ kg\ P\ km^{-2}\ y^{-1}$ ) ( $p < 0.001$ ) (Fig. 4 left), reflecting the contribution of fertilization and trade to the NAPI. Fertilization is the main P input in autotrophic group as shown by the high correlation with NAPI ( $\tau = 0.70$ ). Compared to the heterotrophic group, the P fertilization in the autotrophic group becomes double ( $260\ vs\ 560\ kg\ P\ km^{-2}\ y^{-1}$ ,  $p < 0.01$ ) and its weight observes a five-fold increase (from 20 % to 112 %). At the same time, the NAPI of heterotrophic watersheds is dominated by import ( $\tau = 0.83$ ), which accounts for



**Fig. 3.** Spatial distribution of (A) NANI and N Trade, (B) NAPI and P trade of the investigated watersheds in the Po River district. Negative values (shown on a green scale) mean net exports of N and P trade.

78 % ( $1003 \text{ kg P km}^{-2} \text{ y}^{-1}$ ) of the total net input, which is comparatively higher than the export of autotrophic watersheds ( $-75 \text{ kg P km}^{-2} \text{ y}^{-1}$ ). In heterotrophic watersheds, feed import is the primary driver of P input with  $1123 \text{ kg P km}^{-2} \text{ y}^{-1}$  and it is positively correlated with trade ( $\tau = 0.81$ ), while food is slightly exported ( $-123 \text{ kg P km}^{-2} \text{ y}^{-1}$ ) and it is not correlated with trade. In contrast, in autotrophic watersheds, the P trade is mainly driven by food export ( $-199 \text{ kg P km}^{-2} \text{ y}^{-1}$ ), while no watersheds are feed self-sufficient and the import is  $123 \text{ kg P km}^{-2} \text{ y}^{-1}$  on average. Phosphorus input due to detergents is similar between groups and ranges from 3 to  $176 \text{ kg P km}^{-2} \text{ y}^{-1}$ , representing 2 % of NAPI at the district scale.

Overall, the observed differences in NANI and NAPI composition between heterotrophic and autotrophic watersheds reflect a different N:P ratio of the input, with an average NANI: NAPI ratio in the District of 17, but a higher mean value in the autotrophic group (28) than in the heterotrophic one (13) ( $p < 0.001$ ) (Fig. 4 left).

### 3.3. Nitrogen and phosphorus river loads

Riverine export from the watersheds averages  $1570 \text{ kg TN km}^{-2} \text{ y}^{-1}$  (ranging from 193 to  $4350 \text{ kg N km}^{-2} \text{ y}^{-1}$ ) and  $60 \text{ kg TP km}^{-2} \text{ y}^{-1}$  (ranging from 2 to  $402 \text{ kg P km}^{-2} \text{ y}^{-1}$ ). Inorganic fractions account for 73 % of the TN load (68 %  $\text{N-NO}_3^-$ , 5 %  $\text{N-NH}_4^+$ ), while reactive fractions (SRP) account for 56 % of the TP load (Fig. 6) on average. Mean TN and  $\text{N-NH}_4^+$  loads are higher ( $p < 0.05$ ) in heterotrophic watersheds ( $1661 \text{ kg N km}^{-2} \text{ y}^{-1}$  and  $75 \text{ kg N km}^{-2} \text{ y}^{-1}$  respectively) compared to autotrophic watersheds ( $1115 \text{ kg N km}^{-2} \text{ y}^{-1}$  and  $57 \text{ kg N km}^{-2} \text{ y}^{-1}$  respectively).  $\text{N-NO}_3^-$ , TP, and SRP loads are slightly higher in heterotrophic compared to autotrophic watersheds, but the differences are not statistically significant.

Although TN:TP molar ratios appear to be slightly lower in heterotrophic (with an average of 95:1; min = 17:1, max = 340:1) than

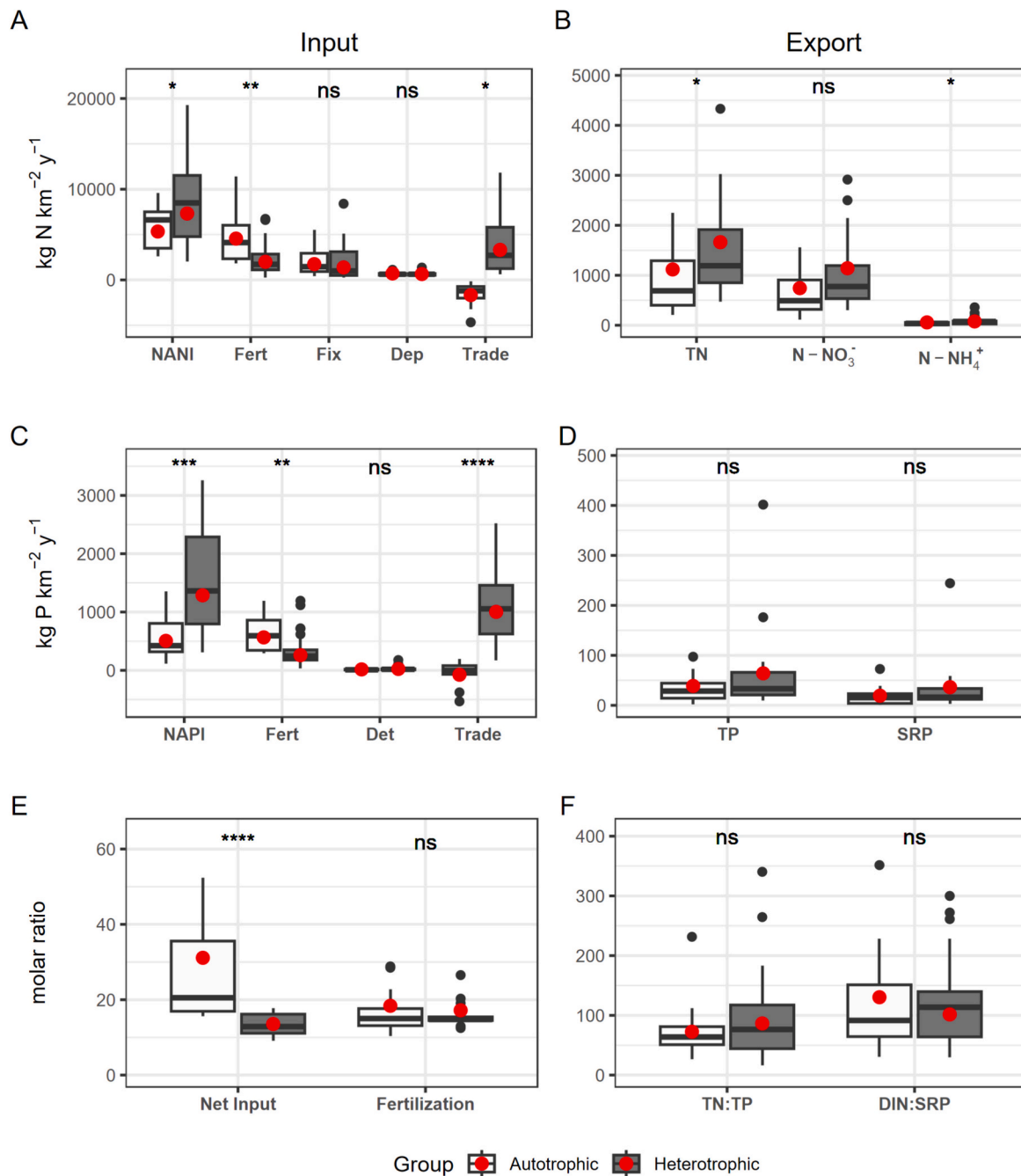
autotrophic (80:1; min = 26:1, max = 231:1) watersheds, the difference is not statistically significant. Similarly, DIN:SRP ratio changes from 120:1 (min = 30, max = 300) to 169:1 (min = 31, max = 654), for heterotrophic and autotrophic watersheds, respectively.

### 3.4. Anthropogenic inputs vs exported loads

The exported TN load is a fraction between 3 and 66 % of NANI, while the TP load is a fraction between 0.2 and 32 % of NAPI. Overall, the catchments retain phosphorus preferentially over nitrogen ( $p < 0.0001$ ), with implications for the stoichiometric ratios between the two elements. Within the trophic groups, the nitrogen exported fraction remains constant; while for P, autotrophic watersheds tend to export a greater fraction (mean = 10 %, min = 0.4 %, max = 32 %) than heterotrophic watersheds (mean = 4 %, min = 0.2 %, max = 15 %), even if this difference is not statistically significant.

The direct relationships between exported loads and anthropogenic inputs (Table S4 in the Supplementary material) shows that the nitrogen MLR characterizes a significant but weak relationship ( $p < 0.01$ ,  $R^2 = 0.17$ ), while the phosphorus and stoichiometry do not show relevant correlations. As a result, we included geo-hydrological variables into the MLR to reassess these relationships, and we tested the same relationships while accounting for the trophic state. All the significant results are shown in Fig. 7, while MLR information is presented in Tables S5 to S7 in the Supplementary material.

The inclusion of geo-hydrological variables significantly improved the predictive power for both nitrogen (TN  $R^2 = 0.76$ ) and phosphorus (TP  $R^2 = 0.59$ ) MLR leading to NAPI significance. All the exported loads are positively correlated with anthropogenic inputs and catchment runoff coefficient ( $C_R$ ), but to a different degree. Total nutrient forms present quite similar patterns, where  $C_R$  is the most important factor influencing both TN (slope = 0.78) and TP (slope = 0.70) exported

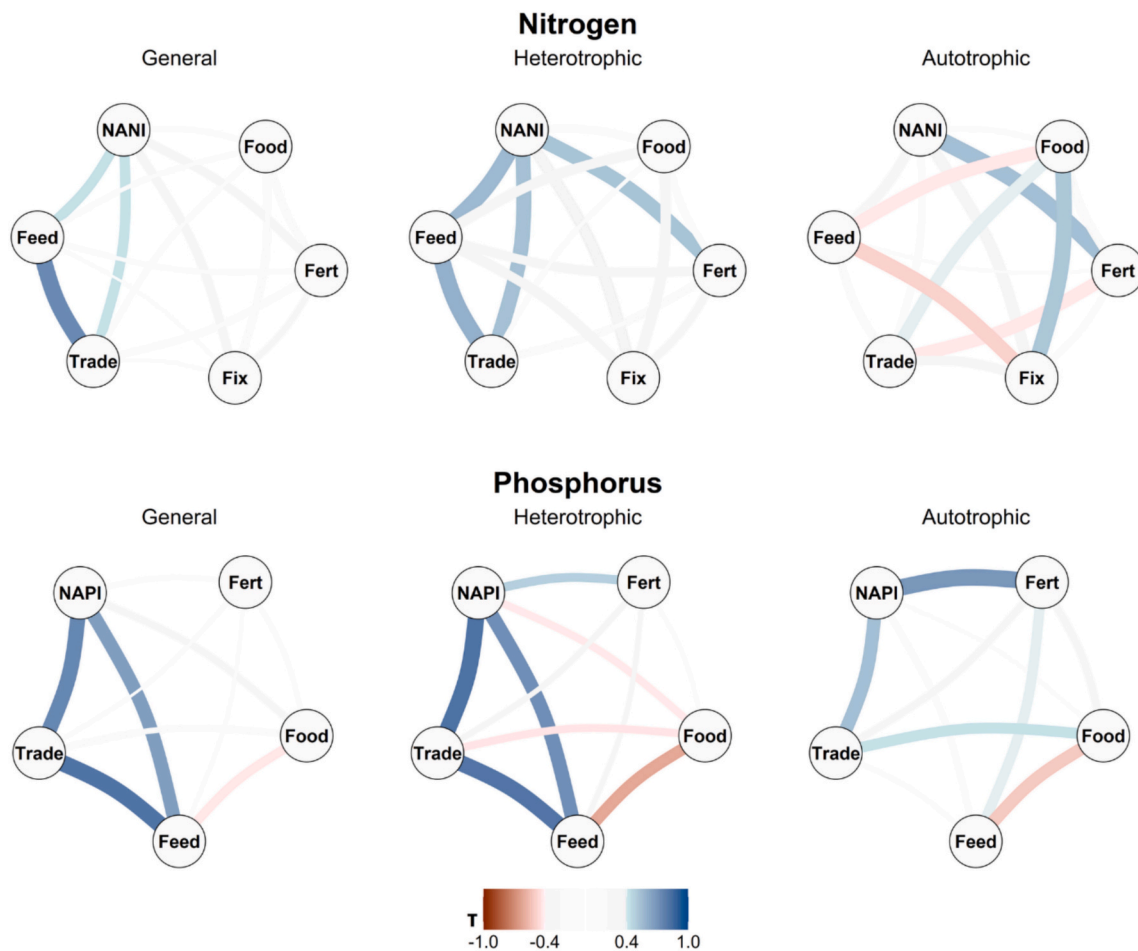


**Fig. 4.** On the left side (A) NANI and its components, (C) NAPI and its components and (E) N:P molar ratio of Net Input, Fertilization; on the right side (B) TN riverine export and its components, (D) TP riverine export and its components and (F) N:P molar ratio of total and reactive forms. The Kruskal-Wallis test ( $p < 0.05$  (\*),  $p < 0.01$  (\*\*),  $p < 0.001$  (\*\*\*),  $p < 0.0001$  (\*\*\*\*), NS (ns)) was used for comparisons among autotrophic and heterotrophic groups. For the autotrophic watersheds, statistical test was executed with absolute values in order to account for the trade magnitude.

loads. At the same time, elevation (Z) is negatively correlated only with TP load. Reactive N forms (N-NO<sub>3</sub><sup>-</sup> and N-NH<sub>4</sub><sup>+</sup>) are equally correlated with both C<sub>R</sub> and anthropogenic inputs, while SRP, similarly to TP, is more dependent on C<sub>R</sub>. This difference is also confirmed by comparing the contribution of NAPI to SRP (slope =  $0.29 \pm 0.14$ ) which is smaller than the contribution of NANI to N-NO<sub>3</sub><sup>-</sup> (slope =  $0.63 \pm 0.11$ ). The stoichiometric ratio of anthropogenic inputs (NANI:NAPI) does not influence the TN:TP ratio. Although Z and PPT have a significant role, they explain only a small portion of the variance ( $R^2 = 0.25$ ). Finally, the MLR for the ratio of reactive N:P was not statistically significant.

The same statistic, but applied only to heterotrophic watersheds, gave different outputs for TN and N-NO<sub>3</sub><sup>-</sup> loads and remains similar for

N-NH<sub>4</sub><sup>+</sup> with respect to the whole dataset statistics. The effect of NANI on TN and N-NO<sub>3</sub><sup>-</sup> loads increases and PPT acquires a significant influence on export but with half the effect of C<sub>R</sub>. On the contrary, NAPI effect on TP load only slightly increases and is the half respect to TN regression (TP slope =  $0.46 \pm 0.22$ , TN slope =  $0.85 \pm 0.11$ ). C<sub>R</sub> and PPT do not show any significant variation compared to the general MLR. Although the SRP export appears to be significantly correlated only with C<sub>R</sub>, the large standard error of the slope associated with NAPI ( $0.44 \pm 0.26$ ) suggests some caution in considering the effect as null. The exclusion of autotrophic watersheds also reveals that in heterotrophic watershed the stoichiometry of the exported loads is negatively correlated to the NANI:NAPI ratio, although the MLR is more significant for



**Fig. 5.** Correlation among the main N and P input components across all watersheds (general and within the heterotrophic and autotrophic groups). For N, correlations are evaluated among NANI, fertilization (Fert), biological fixation (Fix), and trade components (Feed and Food). For P, the analysis includes NAPI, fertilization (Fert), and trade components (Feed and Food). Correlation strength is expressed using Kendall's  $\tau$  coefficient. Values with  $\tau$  between  $-0.4$  and  $0.4$  are masked in white to emphasize stronger associations, while color intensity and thickness of solid lines are proportional to  $\tau$  value.

total ( $p < 0.01$ ,  $R^2 = 0.45$ ) than reactive forms. Among the geo-hydrological predictors, only Z is positively correlated (slope = 0.4) with the TN: TP regression.

Regarding the autotrophic group, MLR models with NANI or NAPI coupled with  $C_R$  result to be the best. Only  $C_R$  has a significant effect on all the forms of nutrient loads, whereas anthropogenic input appears to be uncorrelated. No variables show a significant slope for stoichiometry MLR models.

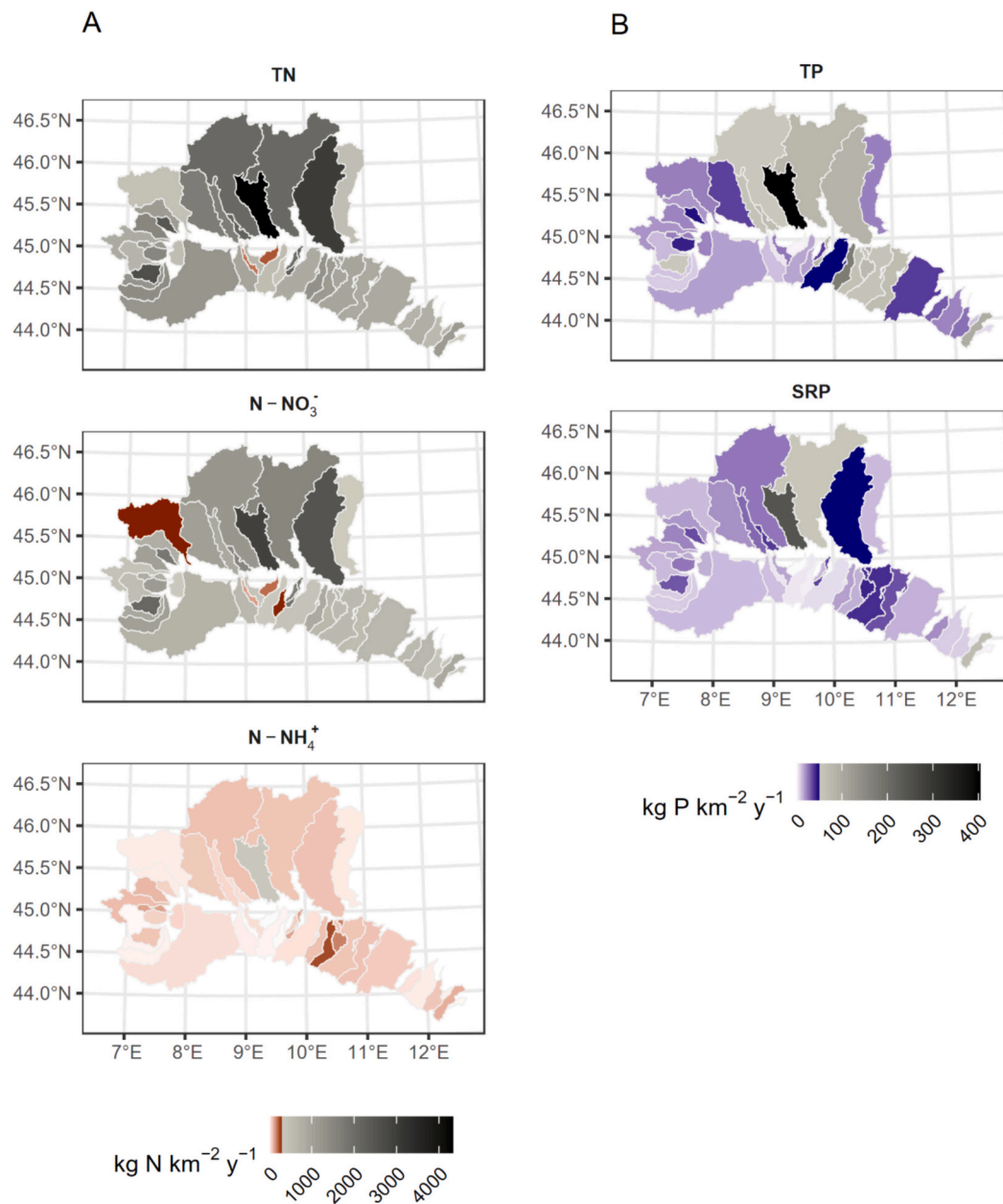
#### 4. Discussion

Historically, a wide range of approaches has been applied to quantify nutrient fluxes within and from watersheds, integrating models of varying complexity with observational datasets (Schoumans et al., 2009; Shan et al., 2023; Swaney et al., 2012). The relationship between net anthropogenic inputs and total (or fractional) nutrient export has been particularly useful for identifying the factors that regulate a watershed's capacity to retain and transform external N and P inputs. This framework offers an effective means to estimate the degree of anthropogenic perturbation on nutrient inputs to watersheds also distinguishing the major sources and, when combined with hydroclimatic variables, provides valuable insights into the mechanisms controlling nutrient export dynamics (Billen et al., 2013, 2010; Goyette et al., 2016; Howarth et al., 2012; Swaney et al., 2012). Geo-hydrological and climatic characteristics of watersheds, such as precipitation, lake density, runoff, altitude and irrigation practices are commonly considered as some of the best

explanatory variables to discern between anthropogenic N and P input and exported load at the watershed output (Goyette et al., 2019; Romero et al., 2021, 2016). Nutrient trade, often separated into feed and food trade, so far has been mainly used to estimate N and P fluxes and their potential impact among countries on a global scale, demonstrating the potential impact of decoupling between exporter vs importer countries on nutrient cycling (Lassaletta et al., 2014b; Wang et al., 2018).

In this study, we explored the novel combination of these two approaches at the watershed scale with the goal of assessing whether the magnitude and composition of nutrient export depend on the interaction between anthropic input type (summarized by trade classification) and geo-hydrological characteristics. The N/P Trade classification acts as a simple filter that statistically defines the dominant system risk. Compared to the simple mass balance approach, our method provides an ecological context that explains how not only the magnitude but also the nature of the pressure contributes to load export. This approach allows us to identify homogeneous groups with distinct export pathways, and it may also contribute to aid the modelling of export dynamics.

The watersheds analyzed in this study are characterized by a combination of a great number of anthropogenic pressures and hydro-geological characteristics. Anthropogenic pressures are among the highest in the Mediterranean area (Romero et al., 2021) and a comparison of the NANI and NAPI measured at world level shows that mean values measured in the HPRD are at the upper end of the range (Table 1). Pressures are generated by the significant development of agricultural and farming sectors that have occurred since the 1950s and by the



**Fig. 6.** Spatial distribution and normalized magnitude ( $\text{kg km}^{-2} \text{y}^{-1}$ ) of exported loads by rivers of the investigated watersheds. (A) Exported Nitrogen: TN,  $\text{N-NO}_3^-$ ,  $\text{N-NH}_4^+$ , with the value of the color change point equal to  $300 \text{ kg km}^{-2} \text{y}^{-1}$ ; (B) exported Phosphorus: TP and SRP exported, with the value of the color change point equal  $50 \text{ kg km}^{-2} \text{y}^{-1}$ .

presence of densely populated urbanized areas such as the cities of Milan, Turin, Bologna, and their suburbs (Viaroli et al., 2018).

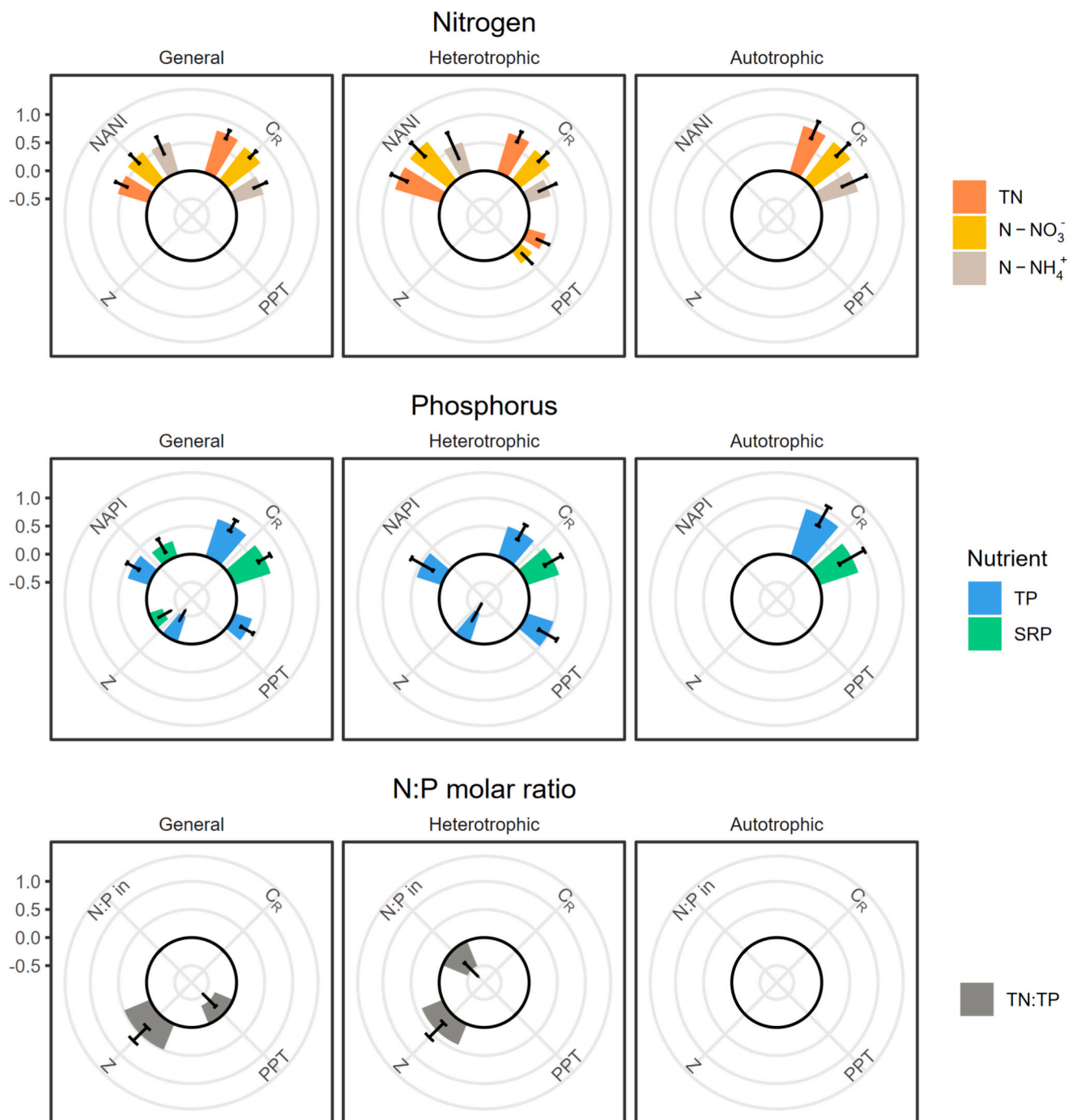
The variability of the exported loads of the different forms of nitrogen and phosphorus was higher than the variability of NANI and NAPI, resulting in highly variable retention capacity among watersheds. In addition, when considering all watersheds, only a weak relationship was observed between NANI and TN, while the effect of NAPI on TP export was not evident. Hydraulic balance, precipitation and mean altitude contribute to explaining N and P riverine loads at the general scale. However, trophic grouping demonstrates that the variability of riverine loads can be also associated with the composition of NANI and NAPI. Within the heterotrophic group, we were able to disentangle the regulating key factors shaping these patterns, while only broader conclusions were possible for autotrophic watersheds due to the smaller number of sites. Trophic separation not only allowed the development of more robust statistics for the heterotrophic group, confirming its unique

characteristics, but also facilitated the identification of stoichiometric relationships. Based on our findings, watersheds appear to exhibit a stoichiometric signature that can indicate the presence and nature of dominant pressures. This concept warrants further investigation and could be extended to include different forms of N and P loads.

#### 4.1. Contribution of different anthropogenic pressures and hydrogeological features to exported N loads

NANI is higher in heterotrophic watersheds than in autotrophic ones, resulting in a corresponding difference in exported TN in rivers. Coherently with Goyette et al. (2023), our findings show that different agrozootechnical systems affect N recycling and export mechanisms.

In the heterotrophic group, feed trade is the most important NANI component, since local forage production cannot meet the N demand from livestock farming. On the contrary, NANI of the autotrophic group



**Fig. 7.** Effect of the tested variables on the exported loads of the different N and P forms. Only significant variables ( $p < 0.05$ ) are reported and presented with a 95 % confidence interval. Bar width is independent from results. NANI:NAPI ratio is abbreviated as N:P in.

is dominated by chemical fertilization due to the feed being mainly exported. These results are not surprising, as many other heterotrophic and autotrophic watersheds share similar NANI characteristics (Billen et al., 2010). This difference is one of the reasons that may explain why the NANI~TN correlation is statistically significant only for the heterotrophic group. Due to the low feed conversion efficiency, most of the N in feed is excreted into manure, contributing to increase soil N surplus. In areas with high livestock density, high N surplus (up to  $180 \text{ kg ha}^{-1} \text{ y}^{-1}$ ) becomes a source of diffuse N pollution which can be easily exported from the watershed by leaching (Martinelli et al., 2018; Pinardi et al., 2018; Soana et al., 2011). This also fits with the differences in TN export observed between heterotrophic and autotrophic watersheds.

DIN does not contribute to this difference which is consequently derived from organic compounds. Organic nitrogen constitutes 75–90 % of the total nitrogen in animal manure (Anon, 2010), confirming the significant contribution of livestock-derived surplus.

Regarding the autotrophic group, the effect of NANI results as statistically not significant. However, it is worth noting that among the autotrophic watersheds, three out of 12 are predominantly cultivated with rice (about 50 % of agricultural land, Table S8 in Supplementary material), and three others are mainly cultivated with alfalfa and meadows with N-fixation that accounts for 50 % of NANI. These two types of watersheds exhibit markedly different N export fractions, ranging from 25 % to 66 % in the rice paddy group and from 2 % to 14 %

**Table 1**

Linear N and P budgets comparison with literature. NANI and NAPI are normalized for the watershed area and expressed in kg N km<sup>-2</sup> y<sup>-1</sup> and kg P km<sup>-2</sup> y<sup>-1</sup>.

Reference	Watershed	NANI	NAPI	N exported	P exported
Billen et al., 2013	European average, 2000	3700	–	811	–
Hong et al., 2012	Lake Michigan Watershed, 1987–1997	3115	–	–	–
	Mississippi Watershed, 1987–1997	2156	–	–	–
Lassaletta et al., 2012	Ebro Watershed, 2000	5118	–	394	–
Goyette et al., 2019	St. Lawrence Watershed (Canada)	609–7885	44–1838	125–1890	9–97
Hong et al., 2017	Danish straits, Baltic Sea, 2010	8779	1251	–	–
	Bothnian Bay, Baltic Sea, 2010	332	31	–	–
Han et al., 2011	Lake Erie watershed (US), 1964–2007	–	28–1438	–	6–80
Han et al., 2014, 2013	Mainland China, 2009	5013	465	–	–
Swaney et al., 2015	India average, 2000–2010	4016	–	–	–
Boardman et al., 2019	Minnesota (US), 2007–2011	–	2–1131	–	3–121
Viaroli et al., 2018	Po River watershed, 2010	1648–26,930	26–4193	1478 ± 375 <sup>a</sup>	34 ± 9 <sup>a</sup>
Romero et al., 2016	Iberian watersheds, 2000–2010	2149–11,634	–	1–2149	–
Zhang et al., 2025	Dawen River Watershed (China), 2000–2021	17,882	5151	–	–
Zhong et al., 2022	Raohu basin (China), 1990–2018	7102	1134	1795 ± 906	151 ± 103
This study	Po River Hydrographic District, 2014–2019	2039–19,258	114–3257	193–4331	2–402

<sup>a</sup> Expressed as DIN and SRP.

in the N-fixation one. In rice paddies, the wet phase promotes NO<sub>3</sub><sup>-</sup> elimination through denitrification, necessitating high N fertilization. In addition, cultivation methods and irrigation practices, from which depend the timing and extent of submersion, significantly influence N export from rice paddies regulating leaching dynamics (Alam et al., 2023; Chen et al., 2022; Omara et al., 2019; Peng et al., 2015). On the contrary, N-fixing crops are generally not amended with N fertilizers and are associated with a high N use efficiency and low N export (Lassaletta et al., 2014a). Therefore, the two cultivation types play a different role in mediating N biogeochemical cycling and when dominant they can influence the N export. It is likely that these watersheds have their own TN ~ NANI relationships, making difficult to find a common one. Nevertheless, these hypotheses were only indirectly verified in our study and should be specifically tested in future research.

In both autotrophic and heterotrophic watersheds, riverine N export strongly depends on hydrological conditions. Together with PPT, C<sub>R</sub>, which indicates the hydrological balance and can be read as a proxy of hydrological connectivity, modulates TN export in heterotrophic watersheds, while it is the sole significant factor in the autotrophic group. It is not a completely unexpected result since the export from agriculture watersheds is largely mediated by hydrological export capacity and by irrigation type (e.g. rainfed crops vs irrigated crops) (Romero et al., 2016). As more precipitation becomes river flow, TN leaching and export increase. Conversely, human demand for irrigation, higher evapotranspiration or water infiltration contribute to stream intermittency and supports nitrogen retention (Lassaletta et al., 2021; Romero et al., 2021; Sarremejane et al., 2022).

Considering N compounds, the hydrological balance is less important for N-NH<sub>4</sub><sup>+</sup> than for N-NO<sub>3</sub><sup>-</sup> in heterotrophic watersheds, as the high solubility of N-NO<sub>3</sub><sup>-</sup> causes nitrogen export to increase linearly with hydrological connectivity through higher rate of soil leaching (Bijay-Singh and Craswell, 2021; Cavallini et al., 2024). Specifically, on the Alpine side of the Po River watershed, higher hydrological connectivity and water availability accelerate N-NO<sub>3</sub><sup>-</sup> leaching from cultivated land to groundwater, further exacerbated by extensive irrigation practices that flood heavily fertilized, manure-enriched soils (Perego et al., 2012; Provolo, 2005; Severini et al., 2024). In contrast, the less-mobile N-NH<sub>4</sub><sup>+</sup> is less influenced by the retention capacity of hydrological networks regulating diffuse sources (Dolph et al., 2019). The exported load of N-NH<sub>4</sub><sup>+</sup> is significantly higher in heterotrophic watersheds than in autotrophic ones, suggesting that this compound originates mainly as excretion from heterotrophic compartments in relation to the activation of secondary sources (e.g. point sources, such as urbanized areas, which are more common in heterotrophic watersheds) (Ehrhardt et al., 2021). PPT also influenced export of TN and N-NO<sub>3</sub><sup>-</sup> only of heterotrophic watersheds, although to a lesser extent than by C<sub>R</sub>. PPT contributes more

to N export in watersheds with a higher water retention (i.e. low C<sub>R</sub>) where land–river connectivity is widely reactivated only during high precipitation (Romero et al., 2021). Therefore, export of N throughout watersheds with low C<sub>R</sub> is driven by flood events triggered by intense rainfall (McDonnell et al., 2021). We identify this hydrological behavior as the key mechanism underlying the differences in nitrogen export between the Apennine (lower C<sub>R</sub>) and Alpine (higher C<sub>R</sub>) regions, marked by contrasting hydrological regimes (Fig. 2; Bard et al., 2015; Cervi et al., 2018).

#### 4.2. Contribution of different hydrogeological features and anthropogenic pressures to exported P loads

NAPI is higher in heterotrophic watersheds compared to autotrophic ones. However, this difference does not directly lead to a corresponding increase in P export. Unlike N, P export remains constant between the two groups, due to the higher retention capacity of heterotrophic watersheds.

Our findings suggest that the combination of livestock farming, manure application, hydrology, and landscape features play a more significant role in regulating P export than the magnitude of anthropogenic input alone. SRP is relatively less mobile than N and tends to accumulate in the soil by binding to metals like calcium, iron, or aluminum (Panagos et al., 2022). Therefore, the primary mechanism for P transfer to aquatic environments is the erosion of particulate forms (Ehrhardt et al., 2021; Kleinman et al., 2011; Menezes-Blackburn et al., 2018). Consequently, P can accumulate in soils for decades, contributing to the P legacy and then be exported, in the form of particulate, with a time lag relative to the input (Dolph et al., 2019). This delay could explain the differences observed in TP and SRP MLRs, where PPT significantly influences TP export but has no impact on SRP. Indeed, in our watersheds about 50 % of the P pool consists of particulate and organic forms.

As a result, we argue that heterotrophic watersheds are more likely to accumulate P than autotrophic ones. Livestock concentration generates more manure for agricultural use, but this is not offset by a reduction in chemical fertilization, resulting in a P excess in soil (Mekonnen and Hoekstra, 2018). Additionally, P export is temporally limited due to its dependence on erosion and precipitation. As a result, in cases of nutrient excess, the system tends to favor accumulation and legacy. However, there is a limit to the P holding capacity of soils and, beyond this limit, further additions of phosphorus will result in accelerated release via run-off (Goyette et al., 2018).

### 4.3. N:P stoichiometry footprint

The different transport mechanisms and rates of N and P through the watersheds modify the stoichiometric ratio between the two nutrients. The role of geohydrological variables, which affects N and P differently, is reflected in an increase in the N:P ratio from a NANI:NAPI of 17 to a TN:TP export of 90. These findings are in line with previous studies indicating a greater relative export of N in comparison to P (25 % for N and 5–10 % for P) (Goyette et al., 2016; Hong et al., 2012; Romero et al., 2021; Swaney et al., 2012).

Although NANI:NAPI is lower in heterotrophic watersheds due to increased NAPI driven by P trade demand, both heterotrophic and autotrophic watersheds exhibit similar TN:TP ratios at the outlet. Phosphorus retention is more pronounced in heterotrophic watersheds, contributing to similar levels of nutrient export between the two groups, and suggesting the influence of secondary factors.

We infer that P imported for livestock feed does not re-enter the agricultural cycle in the same proportion as N. While both N and P are metabolized inefficiently by livestock, P retention is higher (30–40 %) compared to N (5–25 %) in beef and cattle. Moreover, P retention widely depend by excess contained into the feed, since animals preferentially excrete the unused P, while N excretion is more fixed (Pagliari et al., 2020). Consequently, the N:P ratio in heterotrophic watersheds is regulated by two key factors: (1) livestock metabolism and manure management, and (2) the effects of hydrology on P export from cultivated fields. In contrast, autotrophic watersheds, being highly cultivated, are primarily influenced by hydrological dynamics, which regulate the differential transport of N and P.

In the heterotrophic group, we found a negative correlation between the N:P input ratio and the exported TN:TP. This was unexpected and should be interpreted with caution. Based on hydrological controls, we initially expected a positive correlation, where higher N:P input would lead to greater phosphorus retention compared to nitrogen. However, we also found that NANI:NAPI ratio is negatively correlated with P feed ( $\tau = 0.5$ ), a good proxy of livestock density (since the P feed is imported in all watersheds). This suggests that the N:P input ratio in heterotrophic watersheds might be interpreted as a proxy for livestock biomass. A lower N:P input ratio indicates higher livestock density and reinforces the idea of two key control points for N:P stoichiometry, as discussed earlier. When the N:P input ratio increases, also livestock influence decreases, and cropping becomes the main driver of nutrient dynamics.

Interestingly, we didn't find similar patterns in the existing literature. This highlights the need for further research using a larger number of watersheds to confirm our findings. Still, even at this early stage, the trophic classification approach seems promising for understanding N:P stoichiometry.

## 5. Conclusions

This study highlights the interplay between anthropogenic inputs, watershed characteristics, and nutrient export in the PRHD. By integrating the trophic state classification of watersheds within hydrological assessments, we observed that nitrogen and phosphorus exports were not solely dictated by input magnitude, but were also modulated by anthropic input type and varied by nutrient form.

Heterotrophic and autotrophic watersheds exhibit distinct nutrient export mechanisms. In heterotrophic systems, N export is mainly linked to trade-driven feed imports and manure management, while autotrophic systems are more influenced by chemical fertilization, crop type, and hydrological retention. Phosphorus export, however, is less directly linked to NAPI and is largely controlled by erosion, with particulate forms dominating the transported load. Therefore, long-term soil retention might contribute to a legacy effects. At the general scale N:P ratio is subject to the geo-hydrological features which contributes to preferentially export N than P, increasing N:P ratio throughout its pathway within the watersheds. Despite differing N:P input ratios, both

groups reach similar output values, suggesting additional regulatory processes. The presence of two control points (namely livestock and cultivation) in heterotrophic group exacerbates N:P molar ratios, more than the autotrophic group factor which depends solely by crops.

This study first shows that the predictive ability of NANI and NAPI varies across watershed types and not only by their magnitude, emphasizing the need to contextualize input-output relationships. Moreover, N:P input-output regressions preliminary show that stoichiometry can be used as a signature of interaction between hydrology and source type of N and P. Finally, this study offers the first accounts of N and P pollution sources at the PRHD at sub watershed level, providing spatially defined insights for more effective mechanistic modelling and management policies. The sub-watershed approach enables identification and spatial distribution of the specific drivers and can support the development of tailored interventions.

### CRedit authorship contribution statement

**Edoardo Cavallini:** Writing – original draft, Visualization, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Mariachiara Naldi:** Writing – review & editing, Validation, Supervision, Data curation, Conceptualization. **Mattia Saccò:** Writing – review & editing. **Alessandro Scibona:** Writing – review & editing, Resources. **Elisa Soana:** Writing – review & editing, Validation, Investigation. **Pierluigi Viaroli:** Writing – review & editing. **Daniele Nizzoli:** Writing – review & editing, Validation, Supervision, Investigation, Funding acquisition, Conceptualization.

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### Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Edoardo Cavallini reports financial support was provided by Cariparma Foundation. Alessandro Scibona reports a relationship with Po River Basin District Authority that includes: employment. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

Data will be made available on request.

### Acknowledgments

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2025.181030>.

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## Glossary

ARPA: Regional Environmental Protection Agencies

$C_R$ : Runoff coefficient

DIN: Dissolved inorganic nitrogen

LU: Livestock unit

NANI: Net anthropogenic nitrogen input

NAPI: Net anthropogenic phosphorus input

$N-NH_4^+$ : Ammoniacal nitrogen

$N-NO_3^-$ : Nitric nitrogen

PPT: Total precipitation

PRHD: Po River Hydrographic District

SRP: Soluble reactive phosphorus

TN: Total nitrogen

TP: Total phosphorus

Z: Mean altitude