

Review

A Simplified Nitrogen Assessment in Tagus River Basin: A Management Focused Review

Cláudia M. d. S. Cordovil ^{1,*}, Soraia Cruz ¹, António G. Brito ¹ , Maria do Rosário Cameira ¹ , Jane R. Poulsen ², Hans Thodsen ² and Brian Kronvang ² 

¹ LEAF—Linking Landscape, Environment, Agriculture and Food, School of Agriculture, University of Lisbon, Tapada da Ajuda, 1349-017 Lisbon, Portugal; soraiafelix12@hotmail.com (S.C.); agbrito@isa.ulisboa.pt (A.G.B.); roscameira@isa.ulisboa.pt (M.d.R.C.)

² Department of Biosciences, University of Aarhus, Vejlsovej 25, 8600 Silkeborg, Denmark; jpo@bios.au.dk (J.R.P.); hath@bios.au.dk (H.T.); bkr@bios.au.dk (B.K.)

* Correspondence: cms@isa.ulisboa.pt; Tel.: +351-213-653-424

Received: 10 October 2017; Accepted: 27 March 2018; Published: 30 March 2018



Abstract: Interactions among nitrogen (N) management and water resources quality are complex and enhanced in transboundary river basins. This is the case of Tagus River, which is an important river flowing from Spain to Portugal in the Iberian Peninsula. The aim was to provide a N assessment review along the Tagus River Basin regarding mostly agriculture, livestock, and urban activities. To estimate reactive nitrogen (N_r) load into surface waters, emission factor approaches were applied. N_r pressures are much higher in Spain than in Portugal (~13 times), which is mostly because of livestock intensification. Some policy and technical measures have been defined aiming at solving this problem. Main policy responses were the designation of Nitrate Vulnerable and Sensitive Zones, according to European Union (EU) directives. Nitrate Vulnerable Zone comprise approximately one third of both territories. On the contrary, Sensitive Zones are more extended in Spain, attaining 60% of the watershed, against only 30% in Portugal. Technical measures comprised advanced urban and industrial wastewater treatment that was designed to remove N compounds before discharge in the water bodies. Given this assessment, Tagus River Basin sustainability can only be guaranteed through load inputs reductions and effective transnational management processes of water flows.

Keywords: agriculture; impact; measures; nitrogen; Sensitive Zones; Tagus River Basin; Vulnerable Zones

1. Introduction

The European Nitrogen Assessment [1] estimated that around 80% of European freshwaters exceed the nitrogen threshold for high risk to biodiversity and human health. Nitrogen can reach surface waters from point sources, which include municipal wastewater treatment plants and industrial discharges, and diffuse sources, including agricultural runoff of fertilizers and animal wastes, as well as atmospheric deposition. While point sources are relatively simple to regulate since they tend to be a continuous input over time, entering the water body at a specific location, diffuse sources are difficult to quantify and regulate because transport is via hydrologic flow paths and by wet and dry deposition [2].

Agriculture is recognized as a major diffuse source of water pollution [3]. While N fixation, atmospheric deposition and the application of treated sewage sludge can all be important; typically, the major nutrient inputs to agricultural land are from mineral fertilizers and organic manure from livestock [4]. European Union (EU) is a large food supplier and fertilizers are essential to sustain production [5]. High amounts of N are applied in natural and mineral fertilizers as compared to plant

requirements, thus creating N surpluses [3,6]. The magnitude of these surpluses reflects the potential for detrimental impacts on the environment, including upon water quality. N leaching from arable fields to groundwater and surface water contributes to stream N loadings [7–9]. N leaching depends on several factors, primarily fertilization level, type, and timing of fertilizer application; the method of their application to the soil; properties of soils, types of crops and their fertilizer requirements; method of cultivation and agronomic practices; and, the level of animal production [6,10].

While farms represent the smallest operational units at which agricultural management decisions are taken and determining the fluxes of N that are associated with agriculture [11], regional watersheds or river basins, composed of a mosaic of interacting natural, semi-natural, agricultural, and urban landscapes, are the most convenient units at which to describe, but also to manage, the anthropogenic alteration of the N cycle [12,13]. Apart from land use, climatic conditions also have a crucial impact on the intensity and quantity of N leaching at this level [14]. Although certain catchment processes can attenuate much of the nutrient surplus, a significant proportion can still be transported to freshwater, and hence termed an emission. Apart from such reactive nitrogen losses, livestock production and cities metabolism are other sources of N emissions into water bodies [15].

The climatic characteristics play an essential role in the flow regime and influence land uses and water management practices within the basins, both directly and indirectly, being crucial for nutrient transformations and transport [16]. There are several studies regarding water quality in river basins using different methodologies including monitoring, simple mass balance methods, and mathematical modelling (e.g., [17–22]). Nevertheless, river basins in the Mediterranean regions show some particularities that are associated with the semi-arid climatic conditions. In this region, N dynamics has been shown to be substantially affected by flow regulation infrastructures and changes in flow-paths that are related to irrigation facilities [23]. Lassaletta et al. presented an overall N budget in the basin and detailed N calculations in different sub-catchments, within the Ebro River catchment (NE Spain), and hypothesized that agricultural and water management practices had a major influence on N retention [24].

An additional challenge that increases the complexity of N_r control is the transboundary nature of water pollution [25,26]. This is a critical issue in the western part of Iberian Peninsula, where Portugal and Spain share five international watercourses. Indeed, roughly 60% of Portuguese surface waters income from Spain and Tagus River is crucial in that regard, being the longest one. It connects the regions of both countries capitals, Madrid (Spain) and Lisbon (Portugal), being a driving force of social welfare and biodiversity. However, Tagus River Basin is also an outstanding example of water management constraints. An increasing water stress and flow diversion to southern basins are among the most significant ones [27,28]. Besides, although a more consistent delivery of minimum flows has been prescribed in the 2008 amendment of Albufeira Convention, it is doubtful if it is in accordance with ecological requirements of Tagus River. Moreover, both Tagus River Basin Management Plans that were issued in 2015 did not directly address N fate at transboundary level [29]. All of those evidences demand an urgent N assessment at Tagus River Basin scale.

Water resources contamination by intensive agriculture practices and urban wastewaters fostered EU legislative initiatives, respectively Nitrates Directive (91/676/EEC), Groundwater Directive (2006/118/EC), and Urban Wastewater Treatment Directive (91/271/EEC). The first two directives Directive intends to guarantee that nitrates concentration in groundwater remain below a threshold of 50 mg L⁻¹, supporting a low N agriculture footprint. In turn, urban wastewater treatment directive is aiming at avoiding eutrophication processes and imposing stringent limits regarding nitrogen and phosphorus content in urban discharges, thus requiring the use of advanced processes for their removal. Despite these top-down initiatives that are led by governmental agencies, both point and diffuse N pressures remain very significant in European watercourses, according to most recent Tagus River Basin Management Plans [29].

Mathematical modeling contributes more in-depth knowledge regarding complex processes in water management and related N fluxes [30–32]. The quality of primary data and fit for purpose

are the main aspects in model selection and a compromise may be necessary when considering the available time and data. In some cases, experience based analysis and elementary models with few parameters may provide useful information for decision-making purposes in river basin management [33]. A similar approach is used by IPCC (Intergovernmental Panel on Climate Change), 2006 (tier 1), namely for N leaching quantification from manure and soils.

Although there are some articles that are focusing on the environmental issues of individual Mediterranean River basins, and publications summarizing hydrogeochemical and nutrient conditions, a transboundary approach was missing. Thus, aiming at understanding main N transboundary pressures and gap identification, this study provides the first assessment of N_r pressures and responses comprising Portuguese and Spanish Tagus River Basins. First, a general characterization of the Tagus River Basin is presented. Then, the main socio-economic drivers, as well as the anthropogenic pressures in the Tagus River Basin, are identified. The water quality status and the environmental consequences resulting from these conditions are described too. Key policy measures are discussed and sectorial loads are addressed using an emission factor approach. Finally, gaps are identified and recommendations for a better integration of N and water resources management are indicated.

2. The Case of the Tagus River Basin

2.1. General Characterization

Tagus river spring is located in the Albarracín hills in Spain, at a height of 1593 m above sea level. It then flows 1102 km down through Spain and Portugal connecting Madrid and Lisbon on its way to the Atlantic Ocean where it forms one of the world's largest estuaries with 320 km² (Figure 1) [34]. This river flows between the latitudes 40°19'28" N and 38°55'17" N, and the longitudes 1°41'26" O and 9°00'38" O. In Spain, the Tagus Basin holds six main tributaries: Jarama, Alberche, Tietar, Alagon, Guadiela, and Almonte rivers. In Portugal, it receives six tributaries too: Erges, Pônsul, Ocreza, Sever, Zêzere, and Sorraia rivers, being the last two the most important ones due to the size of their river basins (4980 and 7520 km², respectively), totaling around 50% of the Portuguese basin area [34].

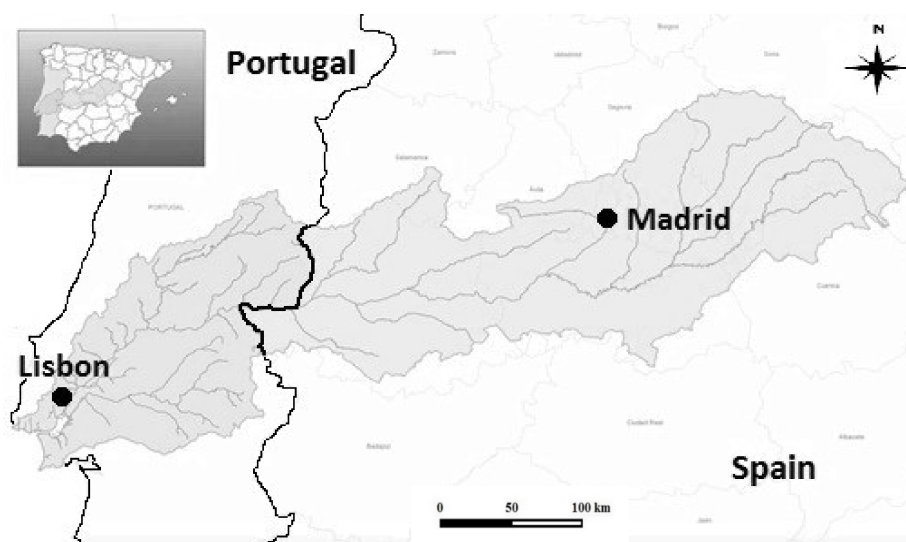


Figure 1. Tagus River Basin in the Iberian Peninsula (built with QGIS) [34,35].

The Tagus River Basin presents an area of 80,500 km². Roughly two-thirds of the catchment are Spanish territory (69%), the remaining one-third is Portuguese (31%) [34]. The climate is temperate Mediterranean, with a dry period of two months for July and August. The average annual temperature varies between 7.4 °C (in areas further north and higher altitude) and 16.9 °C (in estuary area), and the

annual rainfall is between 2744 mm (in the northern part of the region and at an altitude of more than 1300 m) and the 524 mm (in the south, near the coast). In wet years, the annual rainfall is about 130% of the precipitation at normal year, while in dry year, this only reaches about 70% of normal precipitation. The annual potential evapotranspiration varies between around 500 mm in areas further north and the higher altitude, while the higher values, at around 800 mm, are found on the South side of the river basin district. The Thornthwaite climate classification shows great variability, ranging from climate super-wet to sub-humid dry (C1). In natural regime, the average discharge is $600 \text{ m}^3 \text{ s}^{-1}$ and the total volume per year is on average 19 km^3 , with 66% being generated in the Spanish basin and 34% in the Portuguese basin. At present, approximately nine million people live in the basin, which contains the capital cities of both countries. The river is highly regulated with a large number of dams, creating a total storage capacity of nearly 14 km^3 , of which 80% in Spain. Installed hydropower potential amounts to 3300 MW and the mean annual power production is approximately 5000 GWH. In the Portuguese territory, there are almost 2150 dams, providing a theoretical useful storage capacity of about 2.5 km^3 . Most were built for hydropower production, but given the characteristics of hydrological variability, the volumes of water stored in reservoirs add some resilience under scarcity periods [34–36].

The Spanish Tagus Basin attains almost twice the Portuguese Tagus Basin area and number of inhabitants (Table 1). Cultivated area of temporary crops in the Spanish Tagus River Basin is four times larger than that of Portugal [37]. In terms of water demand, 80% of the water use is related to agricultural needs and the 20% remaining for drinking-water production, since both Madrid and Lisbon use the Tagus River Basin as the source of their water supply. Water abstractions for agriculture purposes attain $1929 \text{ hm}^3 \text{ y}^{-1}$ and urban water supply reaches $741 \text{ hm}^3 \text{ y}^{-1}$ in the Spanish Tagus River Basin [34]. In Portugal, Tagus water is strongly demanded for the irrigation ($\sim 1173 \text{ hm}^3 \text{ y}^{-1}$) of intensive rice paddies, orchards and arable crops area (1482 km^2), and for drinking water supply ($\sim 392 \text{ hm}^3 \text{ y}^{-1}$). It should be pointed that Lisbon drinking water is abstracted from a reservoir that is located in a Portuguese Tagus tributary, Zêzere River. Table 1 shows the Tagus River Basin main dimensions and land use characteristics [34,35,37,38].

Table 1. Tagus River and land use characteristics.

Countries	Drainage Area (km^2)	River Length (km)	Total Population (10^6)	Field Crops (10^6 ha)	Trees and Vines (10^6 ha)	Forests (10^6 ha)	Pastures (10^6 ha)
Portugal	25.026	275	3.5	0.4	0.2	0.7	0.008
Spain	55.781	827	7	1.6	0.2	1.25	0.05
Total	80.807	1102	10.5	2	0.4	1.95	0.06

Note: Weighted average according to River Basin area information [34,35,37,38].

2.2. Socio Economic Drivers and Pressures

Economic activities and most of the population in the Tagus River Basin are concentrated in the Madrid and Lisbon areas. In clear contrast to the urbanized areas, the remaining part of the Tagus River Basin is dominated by the use of water for extensive agriculture. Yet, the availability of these resources is disputed by the more productive irrigated agriculture in the Segura River basin that is close to the Mediterranean coastline, and which is connected to the Tagus by a water transfer channel. Indeed, part of the Tagus flow in upper Spain is diverted to the Segura basin for irrigation and food production. This is a main threat on river Tagus sustainability and a very complex pressure to manage, namely during drought events [39].

2.2.1. Portuguese Tagus Basin

Looking to all of the Portuguese hydrographic regions distribution, a stronger concentration of economic activities point out Tagus Basin as hosting more than 55% of the product, activity, and investment, and almost 50% of the existing establishments and employment in Portugal. This is the

largest Portuguese basin representing 31% of the mainland area, 39% of the population, 48% of the employment, and 57% of the production [40].

The urban sector in Tagus Basin is responsible for an annual water consumption of about 297 million m³ (46% of the mainland's total), with an average per capita around 205 L d⁻¹, when considering both resident and a strong influx of non-permanent population. Inside the Tagus Basin, Lisbon is the region with the highest household income (40,090 € y⁻¹). Despite the highest household income in the context of the eight hydrographic regions (1st place in 8) and representing about 39% of the mainland's population, it includes regions of great social fragility [34,40].

In 2012, the agricultural sector represented only 1.1% of Gross Value Added (GVA) (a productivity metric that measures the contribution to an economy of an individual producer, industry, sector, or region) and 2.3% of the employment in Tagus Basin, placing the region in the last position in terms of economic relevance. However, about 40% of the region's total area is dedicated to agriculture, corresponding to 11.221 km² of utilized agricultural area (UAA). The irrigated area counts 148.148 ha (13% of the utilized agricultural area), with around 25,000 farms, corresponding to smaller but more productive farms (for 46% of irrigated GVA only 20% of annual work unit-AWU) than average in the mainland. Economic indicators show that irrigation activity in this region is of much less intensive labor: 0.19 AWU ha⁻¹ when compared to 0.30 AWU ha⁻¹ in mainland, and much more productive: per unit area (144% mainland's mean), per unit work (233% of the mainland's mean), and per unit of m³ of used water (134% of the mainland's mean). The 25,000 mentioned above consume close to 1.173 million m³ y⁻¹ of water (about 34% of total irrigation consumption in the mainland), making the intensity of water use in the agricultural sector higher than in mainland average: mainly per farms (201% of the mainland's values), but per irrigated area unit too (108% of the mainland's consumption per ha), although as seen before water productivity is also higher than mainland's average (134%). Investments in irrigation infrastructure have contributed to improved water storage and distribution capacity, as well as to promote and use precise irrigation technologies, while playing an increasing role to reduce environmental pressures and to adapt to climate change [34,40].

In 2012, industry represented 14% of GVA and 11.5% of employment in Tagus Basin, placing it in the second position in terms of economic relevance. Tagus is the most important industrial basin of the country, with a weight that remained at 36% along the analysed years (2007–2012), with corresponding pressures into the river basin. The annual "product" of energy sector represents about 2% of the Gross Domestic Product (GDP) (a monetary measure of all the finished goods and services produced in a specific time period) of the country. During 2007–2012, this sector registered a strong activity expansion, in contrast with the dominant depressive trajectory, which was reflected in a GVA increase of 19% (annual average of 3.8%) supported by the increase in both turnover (more 38%) and number of establishments (plus 20% between 2008 and 2012). The importance of Tagus Basin in the "energy" sector is distinctly marked in economic terms: it has an overwhelming weight representing between 80% and 90% of GVA and employment volume, placing third in the ranking of the hydrographic regions in terms of hydroelectric power generation, with an average of 12% of the total in 2010–2014. It should be noted that the productivity levels in the use of water and the intensity of its use are qualitatively below the national average [34,40].

In 2012, the tourism sector represented 3.5% of GVA and 8% of employment in Tagus Basin, placing it in the fifth position in terms of economic relevance. Tourism and recreation is associated to various activities related to nature, landscape, and rural areas, linked to historical heritage or cultural and sporting events. Lisbon and surrounding areas plays an increasing role as a tourist attraction and the whole coastline is conducive to new activities.

Aquaculture production that is directly attributable to Tagus Basin has been increasing (274 tonnes in 2011 as compared to 509 tonnes in 2014). About 50% of aquaculture production is an extensive regime, corresponding to less significant pollutant loads as compared to the intensive and semi-intensive regimens [40].

2.2.2. Spanish Tagus Basin

In the Spanish side of Tagus Basin, the densely populated Madrid metropolitan area (6,271,000 inhabitants) has the greatest impact in the region. Here, we find most of the urban water uses, and also the two irrigated areas that are involved in the assessed water transfers [35,39,41]. Madrid registered a population grown by almost 1.5 million people within the last 15 years, from 5,022,000 inhabitants in 1996 to 6,458,000 inhabitants in 2010, at an average annual rate of 2.04%. Population density has also risen from 625 to 805 inhabitants km^{-2} . The attracting power of the Madrid area is explained by the rapid economic growth at an average rate of 3.3% until the end of 2007 [39,41]. Even accounting for three years of economic decline after 2007, GDP per capita had a positive growth rate and increased from EUR 19 755 in 1996 to EUR 23 636 in 2010. In fact, GDP have a mean increased rate around 3% every year resulting in a total GDP growth rate around 60% between 1995 and 2010 (Figure 2). The GVA of Madrid community represents 89% of the total basin Gross Value Added [41]. The main engine of growth up to 2007 was the construction sector but the service sector also grew, and is actually still growing more than average, with a current share of circa four fifths of the regional GDP. Agriculture has never been an important source of growth and its contribution to the overall added value is declining, representing less than 0.6% of GDP (Figure 2). The other potential water user, the manufacturing industry, has being shrinking for more than a decade and its output is nowadays 10% lower than in 2000. The share of the overall regional production has been consequently declining (from nearly 15% in 1995) to less than 9% in 2010 [39].

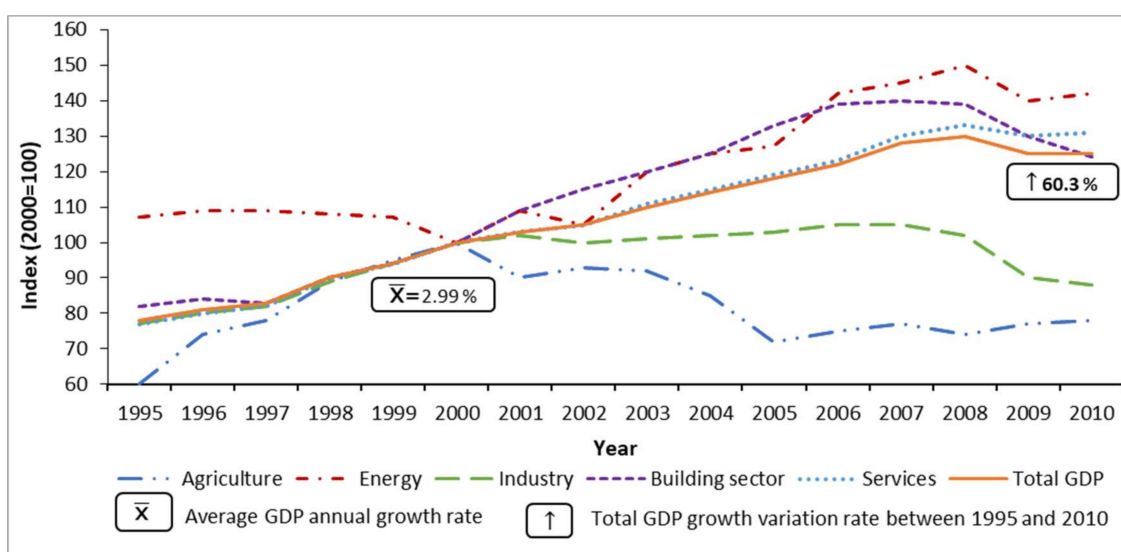


Figure 2. Total Gross Domestic Product (GDP) growth and sectorial evolution, total GDP growth variation rate between the sixteen analysed years and average GDP annual growth rate in Spanish Tagus Basin (1995–2010), chained indexes (2000 = 100) [39].

Economic growth in Madrid was led by the services sector, which explains more than 60% of the total economic growth and 93% of employment generation in the area for the period 1995–2010. The provision of the necessary inputs (such as water) to this sector has laid the foundations to generate most of the economic and employment growth. Agriculture, which is the sector from which water rights are exchanged from, has a minor importance for employment (0.4% of total employment in the region in 2010 and even decreasing during the period 1995–2010), and output (0.1% of total GDP in 2010, also decreasing). Given the low quality of the soils in the Madrid area, agriculture is a receding activity, and, in some areas, water allowances are higher than the effective demand for irrigation water [39]. Allowing for transfers of water rights from agricultural to urban uses may allow for using use water resources that are not being effectively used in the present.

3. Simplified Nitrogen Assessment

3.1. Datasets

Nitrogen data from the ecological potential and status of surface waters in Tagus Basin was obtained mostly from the last River Basin Management Plans reports. In Portugal, these plans were reported by the Portuguese Environment Agency (“Agência Portuguesa do Ambiente”, APA) [34], while in Spain, they were reported by the Spanish Hydraulic Administration (“Confederación Hidráulica del Tajo”, CHT) [35]. Datasets about monitoring stations and reservoirs in Tagus Basin, regarding total N and NO_3^- concentrations were obtained from CHT [42] for Spain and from SNIRH, a National Water Resources Information System [43], for Portugal. Portuguese geographic files used in QGIS were taken mostly from SNIAmb data (National Environmental Information System) of Portuguese authorities [44]. Spanish maps were adapted through the online GeoPortal (access portal to geographic information of Spain), which uses IDEE data (Infraestructura de Datos Espaciales de España) of Spanish authorities [45].

Potential N loads in Tagus River Basin were estimate using available emissions factors, datasets, and statistics that were published in Decree-laws. Agriculture diffuse N loads to surface waters were estimated according to land use information from the Corine Land Cover [37] and emission factors of agriculture practices [46] (Table 2).

Table 2. Nitrogen export coefficients, according to agriculture practices.

Sources	Sub-Categories	Emission Factors ($\text{kg N}_r \text{ ha}^{-1} \text{ y}^{-1}$)	Ref.
Agriculture practices	Temporary rainfed crops, irrigated crops and rice paddies	5.0	[46]
	Vineyards, orchards, olive grooves	2.7	
	Permanent grassland	1.5	

N loads originated by livestock production were based on the Portuguese agricultural census that was carried out by the Portuguese national statistics institution (INE) [47] and on the Spanish CHT data, based on the Impress II data of Corine Land Cover and livestock facilities inventories [35]. Excretion factors and correspondence normal head were taken from the Decree-Law 214/2008 of 10 November (republic diary number 218) and Ordinance 259/2012 of 28 August (republic diary number 166), both in force in Portugal.

For the urban sector, *per capita* N discharge factors used were the ones reported by Johnes [33] regarding urban Wastewater Treatment Plants with biological secondary processes and on-site anaerobic septic tanks: 2.14 and 2.49 kg N y^{-1} , respectively. An additional removal efficiency of 86% was considered if the advanced biological processes are implemented [48].

3.2. State and Impacts: Water quality status in Tagus River Basin

Nitrates are considered in Water Framework Directive Annex VIII [29], and they belong to physico-chemical parameters that are required for an integrative ecological status assessment. Figure 3 shows surface waters ecological potential along Tagus River Basin and the two N monitoring points used.

In the Spanish part of Tagus watershed, 63% of rivers and 71% of lakes present Good ecological status, 31% of rivers and 29% of lakes present Moderate status, and 6% of rivers display Poor status. Concerning the ecological potential, 59% of the artificial/heavily modified water bodies display Good or Higher status, 35% Moderate status, and 2% Poor status (4% remain unknown). For groundwater bodies, 75% are classified with Good Global status and 25% have Less than Good [35]. Concerning the Portuguese part (including the west side), 53% of surface water bodies have Good ecological status, 26% Moderate status, and 21% Poor status. As for the ecological potential of artificial/heavily modified water bodies, 14% present Good status, 46% Moderate status, and 27% Poor status (13% remain

unknown). For groundwater bodies, 90% are classified with Good Global status and 10% have Poor classification [34].

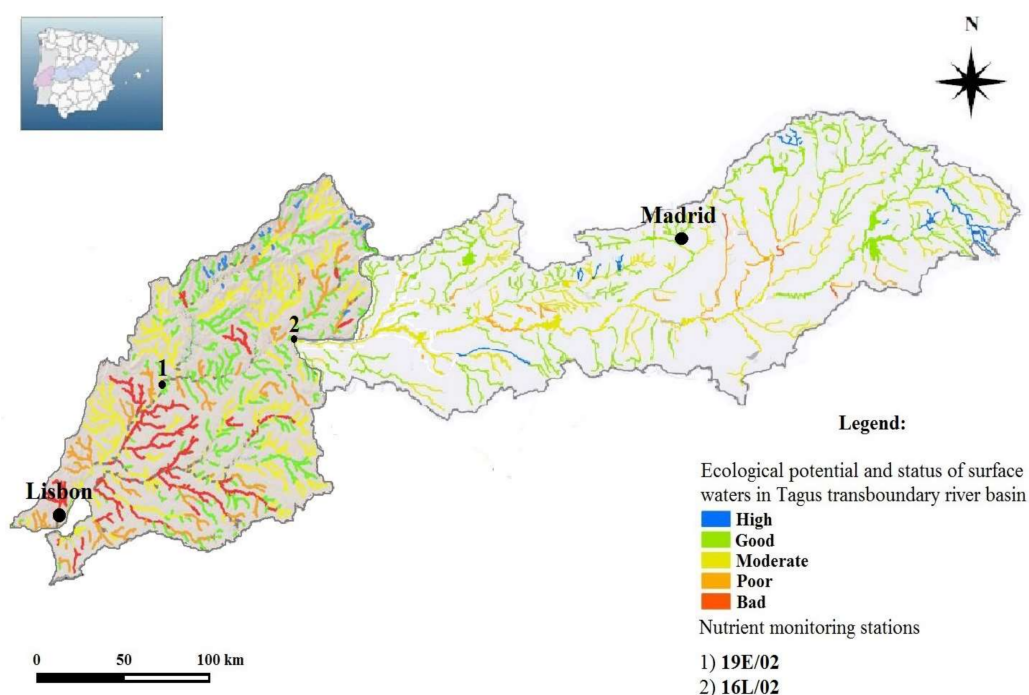


Figure 3. Surface waters ecological potential and status along Tagus watershed reported in 2015. N monitoring stations: (1) “Valada do Tejo” (code: 19E/02); and (2) “Monte Fidalgo – Cedillo” (code: 16L/02) (built with QGIS) [34,35].

3.3. Nitrogen Loads in Tagus River Basin

3.3.1. Livestock

N loads derived from livestock activity were estimated from the average amount of nutrients that were excreted annually by “normal head” for each animal species and after having the normal head numbers per specie and per parish (only parishes with 50% or more of land within the Tagus Basin were considered), total N load was estimated based on the average amount of total N that was excreted annually by normal head. Calculations taking account that the N loads emitted by manure vary according to the animal category, species, nutritional habits, and weight of the animal, along with manure management characteristics [49]. An average concentration of 25 g N kg^{-1} in manure was considered [50]. Finally, to determine N leaching into water bodies, after manure deposition in the soil, an approach consisting in export taxes was used. These taxes range from a mean for N around 10–17% considered by different authors [33,51,52]. It was assumed that 17% of the N load reaches the water bodies of the river basin where the livestock farm is located, and already take into account the percentage of manure that is applied on land after storage losses [33]. In Portugal, around 9% of the total holdings with livestock have manure storage facilities, while in Spain, this percentage is almost four times higher (~44%) [53].

3.3.2. Agriculture

The methodology that was used to estimate N loads from agriculture was based on emission factors for each land use classes, corresponding to the diffuse N load that will be transported through the surface runoff from the drainage area for each water body. Identification and spatial distribution of land use classes in the Tagus Basin were determined using the land use map [37], which allowed

for the use of a geographic information system (QGIS) to define the exact percentage of each land use classes. Then, N export coefficients [46] were applied to these percentages of land.

3.3.3. Urban

The approach used to determine the rejected N loads was based on removal coefficients, according to Wastewater Treatment Plants performance. Most of these urban treatments existing in the Tagus Basin have secondary treatment only (80%). The more advanced treatment has also disinfection or a N removal step. Tagus Basin has about 14% of this treatment degree. Urban wastewater discharges without treatment were considered to be 8% in Portugal and 4% in Spain [54]. Annual N load at the international border between Spain and Portugal was estimated based on the “Monte Fidalgo–Cedillo” reservoir (Figure 3) monitoring between 2010 and 2015 and considering an annual average flow of $210 \text{ m}^3 \text{ s}^{-1}$ at “Monte da Vinha”, which is a hydrometric station located too on the border between Portugal and Spain [42,43].

3.3.4. Intersectorial Assessment

As mentioned previously, N pressure to surface waters derives mostly from agriculture and urban settlements in the Portuguese Tagus River Basin. On the contrary, in the Spanish Tagus River Basin, the main challenge is potential livestock emissions: estimated N load into Spanish Tagus river is $\sim 242 \text{ kt y}^{-1}$, which is much higher (~ 13 times) than Portuguese discharge, only $\sim 18 \text{ kt y}^{-1}$. The main contributor to N losses in Portugal is agriculture (Figure 4), while in Spain, it is livestock, which is more than 50 times higher than in Portugal. N pressures in urban and agriculture sectors in Spain are higher than in Portugal too. Riverine export from Spain to Portugal (14 kt y^{-1}) is slightly smaller than the total N load discharged from the three main sectors in Portugal (18 kt y^{-1}). However, only 3 kt y^{-1} is discharged into the estuary (Figure 4). The estimates of potential N loads from different sectors contribute to set up a simplified N mass balance along Tagus River Basin, which is depicted in Figure 4.

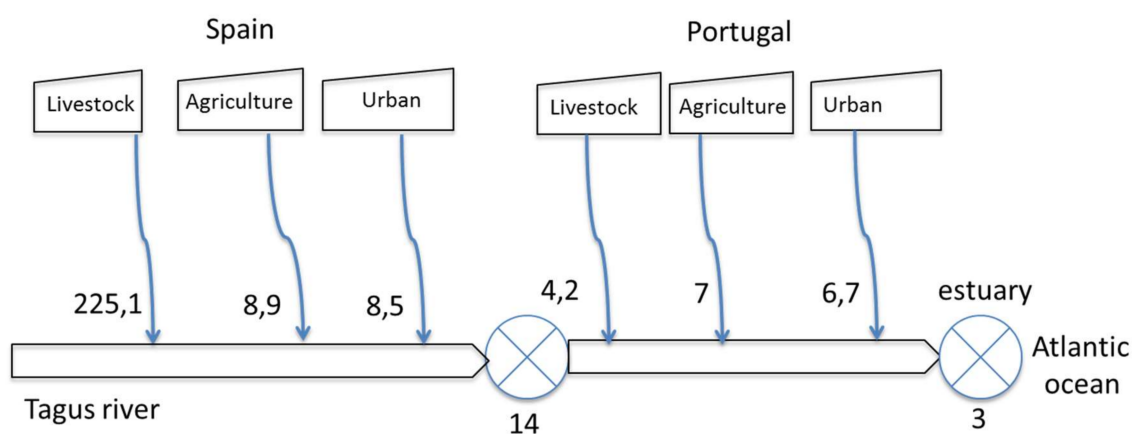


Figure 4. Estimated potential N loads (kt y^{-1}) into Tagus River Basin surface waters per sector (livestock, agriculture, and urban), pressure at the Spain/Portugal border, and the discharge at the Tagus River estuary, in Atlantic Ocean for 2009–2015 [34,35,37,42,43,54].

This integrated N assessment of Tagus River Basin confirms the presence of significant challenges in both countries, Portugal and Spain. However, their magnitude is different. Agriculture, livestock and urban sectors discharge higher N loads in Spanish Tagus than in the Portuguese Tagus. Livestock is the most important sector, but, while Portuguese reports a livestock density of 1.1 ha^{-1} per hectare, Spain reports values that are ten times higher, $11.4 \text{ units ha}^{-1}$ [35] that is spread along a higher area, leading to a global livestock load that is ~ 120 times higher than in Portugal [35,47]. Thus, when

considering the same N exports coefficients in both countries, one could expect water body's quality to be the worst in Spain. However, this is not the case. One reason may be the type of livestock holdings and the number of manure storage facilities that are much higher (~4 times) in Spain than in Portugal [53]. Good manure management practices and effective wastewater treatment may support Spain's good ecological quality status (Figure 3). In terms of agricultural N loads, the difference in crop area in both of the countries explains the higher magnitude in Spain, e.g., for temporary crops. Finally, regarding the urban sector, it could be expected that Spain displayed a higher N load than Portugal because of a higher population (Table 2). This effect is attenuated by an increased N removal that is imposed by an extensive Sensitive Zone designation, which aims at a significant pressure reduction from Wastewater Treatment Plants loads.

Regarding N loads pattern in Portugal in 2014 [55] and when compared with the values that were estimated in the present work, it is possible to identify an important livestock load increase (~2.5 to 4.2 kt y⁻¹), while agriculture had a slight rise only (~6.5 to 7 kt y⁻¹) and the urban sector a significant shrinkage (~12.9 to 6.7 kt y⁻¹). In fact, according to Portuguese National Statistics [47,56], animal production in 2015 increased in all sectors (meat, eggs, milk, and processed dairy products). Production of livestock meat increased by 5.0% in 2015, a general trend extended to all livestock species. Not so pronounced, but with a similar trend too, is the N net balance in the soil with 100,000 tonnes of N in 2015, which is equivalent to 27 kg N ha⁻¹ of agricultural area (26 kg N ha⁻¹ in 2014) [56]. When compared to 2014, N net balance increased by 4.6%. This evolution was justified by the increase of 2.3% N incorporation in soil when compared to 2014 (more than 7.2 thousand tonnes of N), in particular due to the incorporation of manure in the soil (more 2.6%). On the other hand, in 2015, the N removal from the soil by agricultural crops, fodder, and pasture increased by 1.6% (more 2.8 thousand tonnes of N) [47,56]. Between the two periods, total N_r pressure in Tagus River Basin decreased substantially in Portugal (22 to 18 kt y⁻¹). Several reasons can contribute to such a decrease, but data reliability is not very conclusive. Nevertheless, a main reason could be the gradual improvement of wastewater treatment services [34].

3.4. Total Nitrogen, Nitrate Fate and Transboundary Pressures

A downward trend of the Total N concentration was observed in Portuguese-Spanish border at "Monte Fidalgo" monitoring station from 2013, although there was an increase in NO₃⁻ N concentration in 2015, probably from agricultural activities intensification. Between 2010 and 2015, the total N concentration was always higher in the monitoring station "Valada do Tejo" than in the upstream station (Figure 5B). In 2015, total N concentration dropped significantly below the detection limit that was reported by CHT, which is 2 mg L⁻¹ for total N and 2.5 mg L⁻¹ for nitrates [35]. Until 2012, nitrate concentration in "Valada do Tejo" was smaller than "Monte Fidalgo" (Figure 5A). In 2013, it remained the same for both stations, and, since then, "Monte Fidalgo" recorded values below the other station with significance differences in 2015. In order to assess transboundary impacts, average total N and NO₃⁻ concentrations in the two N monitoring points of Tagus River Basin are displayed in Figure 5.

Water quality monitoring in Tagus mainstream shows a biased pattern. For the study years, "Valada do Tejo" has higher N concentration than upstream "Monte Fidalgo", but the same did not happen with NO₃⁻ concentration, being more expressive in 2011 and 2012, possibly because the intensive agriculture that occurs at Valada Zone (Figure 5). As a rule, N concentration in the Portuguese-Spanish border of Tagus is around 1 mg L⁻¹, which is probably due to the contribution of Tagus tributaries near the border causing a dilution effect (e.g., Alburrel, Aurela and Salor streams) and to the N consumption in Alcántara and Cedillo [57]. Annual riverine export monitored in Spain-Portugal border is still high (14 kt y⁻¹) (average 2010–2015), an amount similar to the N discharged downstream by Portuguese agriculture, livestock, and urban sectors (~18 kt y⁻¹). The difference in source discharges and transport at border and final input at coast attains 94% in Spain and 91% in Portugal and in total for the entire Tagus Basin is 99%. In Denmark, the national

average N retention in groundwater and surface water accounts to 72% from source to coast. Biological reaction may be the reason, as several reservoirs exist along Tagus River: higher hydraulic residence times and warmer climate with excess carbon could fuel denitrification in the surface waters. These results show that the monitoring gaps in Tagus Basin are quite important regarding N fluxes, thus hindering a comprehensive calibration of any phenomenological model. Better information on water quality coupled with surface and groundwater fluxes quantification, besides biological activity and atmospheric emissions, are necessary. In addition, N fate in Tejo estuary could be also meaningful to induce anoxia in coastal areas, but the issue has not been addressed yet.

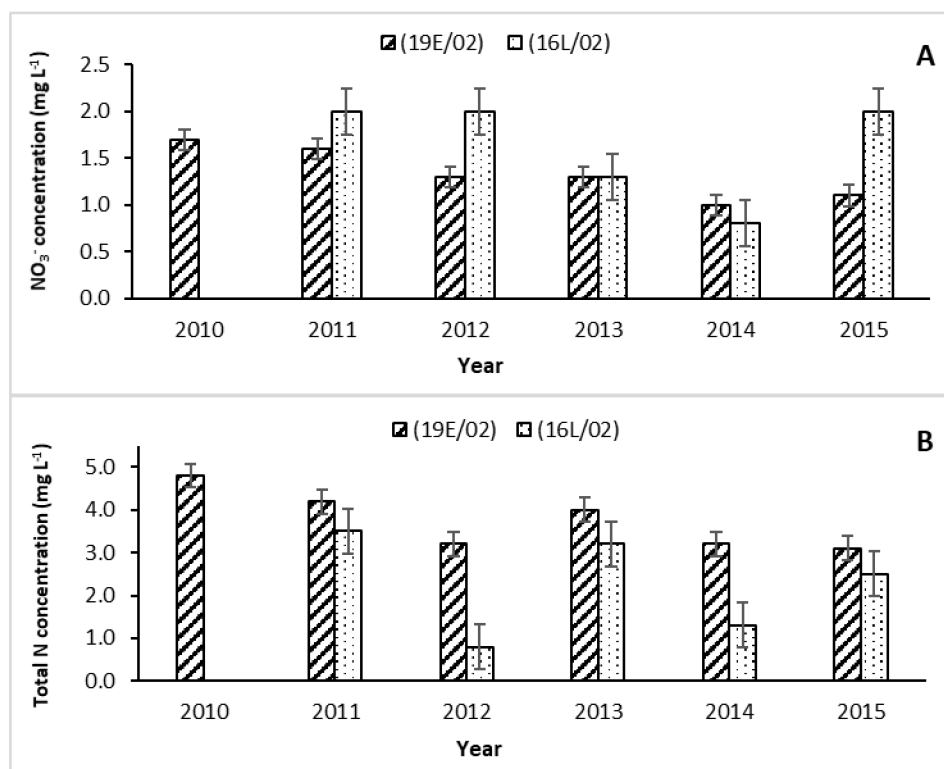


Figure 5. Average NO₃⁻ (A) and total N (B) concentration (mg L⁻¹) in Tagus River Basin between 2010 and 2015. (Monitoring stations: code: (19E/02)—“Valada do Tejo”; code: (16L/02)—“Monte Fidalgo”) [42,43].

4. Policy Measures

Despite the fact that Tagus is an international basin, each country issued its own Management Plans in 2015 and not an international one, as foreseen by Water Framework Directive in its article 13(2). Even so, the Programme of Measures foreseen in both Tagus River Basin Management Plans comprises a set of initiatives that are related with N issues [34,35]. Among them are agriculture best practices and further wastewater treatment upgrade for nutrient removal. The 2016–2021 planning cycle is expected to spend 229 M€ for Programme of Measures implementation in Portuguese Tagus River Basin Management Plans, including 174 M€ specifically for sanitation and pollutants removal [58]. To achieve a decrease of diffuse and point sources in Spanish Tagus River Basin for the same planning cycle will require a higher investment in N control than in Portugal, 1.452 M€ [35].

Besides the initiatives that were encompassed in Tagus River Basin Management Plans, an effective cooperation between Portugal and Spain is necessary in accordance to Albufeira Convention goals. Although a joint co-management is difficult, some steps could be implemented, such as, for example, joint best agricultural management practices for the entire Peninsula, including the appropriate measures for the edafo-climatic common regions. In the Programme of Measures definition, a cost-effectiveness

analysis will be advisable in order to find the best upstream-downstream measures [59]. Joint monitoring systems would be a step ahead for achieving water quality compromises [60], as well as a common interpretation of the EU Directives. Above all, transparency and a far-reaching coherence regarding the policies in Tagus transboundary river basin is required in order to prevent negative trade-offs [61].

4.1. Nitrogen and Water Resources Protection Policies: Protected Areas

Nitrates Directive (91/676/EEC) and Urban Wastewater Treatment Directive (91/271/EEC) are central EU legal tools embedding anticipative water management policies. In Portugal, the first legal initiative on groundwater protection was issued in 1997, with the release of Decree-Law 235/1997 of 3 September (republic diary number 203). Ground waters with more than 50 mg L⁻¹ of nitrate concentration are considered to be Vulnerable Zones [62]. Tagus Nitrate Vulnerable Zone was implemented only in 2004 through the publication of Ordinance 1100/2004 of September 3 (republic diary number 208). This Nitrate Vulnerable Zone covers ~36% of river watershed and is the largest one in the country, with a total area of 2416.86 km². The other Nitrate Vulnerable Zone was Estremoz-Cano issued in 2010 through the publication of Ordinance 164/2010 of March 16 (republic diary number 52) and attains 207.1 km². In both cases, an intensive agricultural activity is present, namely maize, tomato, and rice [62]. Despite such measures, from 2012 to 2015, more than 50% of monitoring data stations recorded a nitrate concentration average value of 36 mg L⁻¹ and less than 25% recorded an average value of 44 mg L⁻¹ in aquifer (0–5 m) of Tagus Vulnerable Zone. In the karst aquifer of the Estremoz-Cano Vulnerable Zone, more than 50% stations registered an average of 37.5 mg L⁻¹ during the same period and less than 25% registered an average of 12.5 mg L⁻¹ [34,62]. In Spain, 7 Vulnerable Zones that spread 31% of Tagus watershed area (17,064 km²) are in force [35,63]. Vulnerable Zone effectiveness is controlled by 46 network stations. From 2008 to 2014, five groundwater bodies presented at least a representative point of analysis above 50 mg L⁻¹. This accounts for 50% of total groundwater bodies [35,63].

Regarding Sensitive Zones in terms of nutrients and eutrophication risks, only in 2008 the first zones were designated in Portuguese Tagus: Pracana and Maranhão reservoirs and associated watersheds, covering 13% of the Tagus River Basin (Figure 6) [34]. On the contrary, a stronger policy was adopted in Spain, namely downstream Madrid region: 53 Sensitive Zones were identified that influence areas to a sum total of 32 815 km² (60% of the river watershed) require biological N removal in wastewater treatment plants [63]. Vulnerable and Sensitive Zones along the Tagus River watershed are shown in Figure 6.

Portuguese water authorities are concerned with nitrate concentration in the Tagus Vulnerable Zone [62]. Regarding the Estremoz-Cano Vulnerable Zone, the Action Program, which was issued by Portugal in Ordinance 259/2012 of 28 August, may induce a water quality improvement in the next 10 years [62]. On the other hand, Vulnerable Zone in Spain Tagus does not go through this problem despite some records of nitrate contamination [35]. The effectiveness of the designation of large Sensitive area in Spain (53 zones) seems evident by the water ecological status in the Spanish Tagus River Basin [63]. This is a good result that deserves further considerations because other European countries apply environmental protection policies with similar results. For instance, the whole Denmark territory is designated as a Nitrate Vulnerable Zone, and due to the application of stringent wastewater treatment removal (N and P) over all of its territory, Denmark was not required to identify Sensitive Zones for the purposes of the Directive [29,64]. The good water status goal has been achieved in Spain, despite a highly regulated water flow regime in Tagus headwaters, namely the aforementioned water abstractions towards Segura and Jucar river basins (Figure 3) [65]. Such water transfers to adjacent river basins from upstream Tagus River Basin supported strong debates over pros and cons, confronting the agricultural needs in Spanish southeast zones with nature conservancy goals in Tagus River Basin, including in Portugal [66].

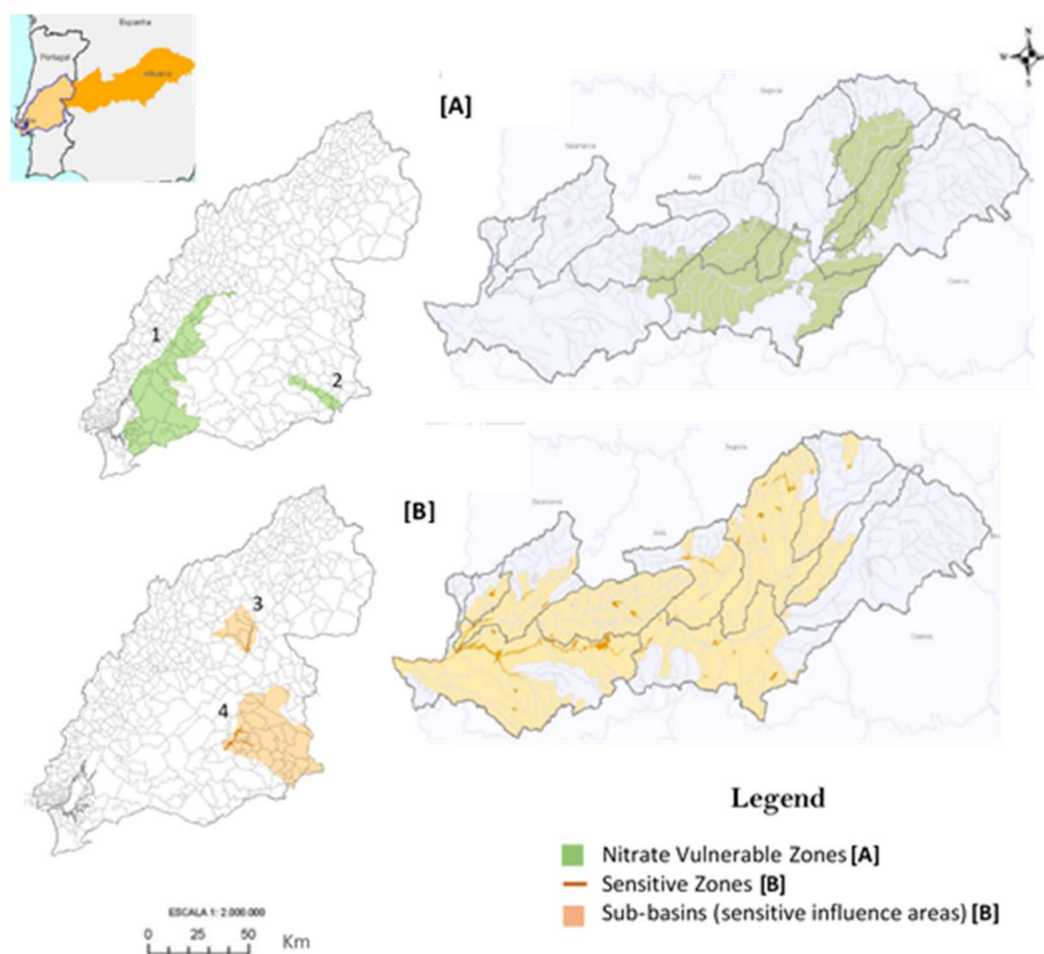


Figure 6. Nitrogen Vulnerable [A] and Sensitive [B] Zones in the Portuguese and Spanish sides of the Tagus River Basin (built with QGIS) [34,35,44,45]. Numbers correspond to Portuguese Tagus sections of Vulnerable (1-Tagus; 2-Estremoz-Cano) and Sensitive (3-Pracana reservoir; 4-Maranhão reservoir) Zones.

4.2. Best Management Practices

The Water Framework Directive [29] and its daughter Directives recognize the urgent need to adopt specific measures against the contamination of water by individual pollutants or a group of pollutants that present a significant risk to the quality of water. There are some useful tools and techniques that can be used by farmers, technicians or government entities to improve their knowledge and mitigate this problem on Tagus Basin.

One of them is the use of mathematical models to assess the fate of N in the soil–crop environment from the field to the watershed scales. The Root Zone Water Quality Model (RZWQM) [67–69] was already successfully used at the field scale in some areas of the Tagus basin. The model simulates N transformations, uptake, and transport in the soil–crop systems, making it possible to evaluate field measured soil hydraulic properties and to predict N related variables for different boundary conditions (irrigation and fertilization) with a good accuracy. Thus, through scenario analysis, the best management practices that were protecting surface and groundwater quality can be selected. As for every process based mathematical model, each time that RZWQM is used in a new soil–crop system, it has to be calibrated. Despite this, it is essential to first have a good estimation of the water balance components (evapotranspiration, leaching, and soil water storage) before applying the model [68].

Researchers of the Marine Research Institute, an ecological modelling center in Portugal, have demonstrated that salt marshes vegetation could be a great attenuator of the effects of N enrichment in

several coastal systems, like in the Tagus estuary, and used as a measure of the system susceptibility to nutrient enrichment [70]. Their model results show that after phytoplankton, salt marsh plants have the highest productivity in the estuary. The model also suggests that the Tagus estuarine sediments act as a source of ammonium to the water column, but that its diffusion flux is minimized by the growth of salt marsh plants. So, the ammonium diffused to the water is reduced by about 15% in the Tagus salt marsh sediments.

Not only models can be a useful tool for N control. Probability maps, showing that the nitrate concentrations exceed a legal threshold value in any location of the aquifer, can be used to assess risk of groundwater quality degradation from intensive agricultural activity in aquifer. The DK (Disjunctive Kriging) technique is an example of that mapping type. These kinds of tools are very useful for the decision-makers because they can reinforce the implementation of agri-environmental measures in Vulnerable Zones, so as to ensure good compliance with the Nitrate and Groundwater Directives in the EU zone [71].

5. Conclusions

Nitrogen pollution from agriculture, livestock, and urban discharges is a key environmental pressure on the Tagus River Basin. Nitrogen load in Spain is ≈ 13 times higher than in Portugal, being the livestock sector the major input. Nitrogen concentration in the Spanish Tagus River is low, but the input to Portugal is significant (14 kt y^{-1}), accounting for approximately the same amount as the total sectorial load in the Portuguese region (18 kt y^{-1}). However, reported water quality status was slightly better in Spain than in Portugal. Around 67% of natural surface waters (63% of rivers and 71% of lakes) showed good ecological status, while for Portugal, this status accounted for only 53%. Gaps in monitoring hinder the construction of a comprehensive mass balance at basin level and foster data uncertainties that hinder an integrated water resources management.

The main policy responses to N pressures are related to the designation of water resources protection areas in both countries. In Spain, Sensitive Zones attained 60% of Tagus River Basin area, while in Portugal, these are limited to 13% of the basin. Vulnerable Zones attain near 30% of the territory in both countries, but the enlargement of these zones could be beneficial in terms of water quality in both countries. Iberian countries administration of their own Tagus water resources is driven most by water security reasons and not by benefits sharing in water and agriculture related activities. Stronger collaboration was though by Water Framework Directive aiming at a shared effort to attain environmental objectives for transboundary waters. The adoption of Best Management Practices built under a common strategy, would help to control and mitigate the nitrate problems in the Peninsula. A joint systematic information exchange and interaction will lead to a better transboundary N management and water resources protection in the Iberian Peninsula.

The simplified methodology presented in this paper allowed for analyzing and characterizing the current state of the Tagus Basin and understand the main driving forces and responses. Nevertheless, for a more comprehensive analysis of the N processes and dynamics at the basin level, a process-based model is being developed and will be presented in a near future.

Acknowledgments: The authors acknowledge NitroPortugal, H2020-TWINN-2015, EU coordination and support action n. 692331 for funding. Authors would like to thank APA Portuguese Environmental Agency support, in particular Felisbina Quadrado, and Sofia Batista. Guilherme Gonçalves is acknowledged for the participation in the initial data collection and first figures elaboration.

Author Contributions: Cláudia M. d. S. Cordovil, António G. Brito, Maria do Rosário Cameira and Soraia Cruz have written, coordinated and reviewed the paper and finalized the data collection. Soraia Cruz reviewed and corrected all the data for all the necessary calculations within the N assessment in the river basin along both countries, to ensure the accuracy of the numbers presented in this paper, and redraw paper figures. Jane R. Poulsen, Hanns Thoden and Brian Kronvang contributed to refine the paper structure and to improve the scientific aspects, as per their twinning role in the NitroPortugal project.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Sutton, M.A.; Howard, C.; Erisman, J.W.; Billen, G.; Bleeker, A.; Grennfelt, P.; Grizzetti, B. Assessing our Nitrogen Inheritance. Chapter 1. In *The European Nitrogen Assessment Perspectives*; Sutton, M., Howard, C., Erisman, J.W., Billen, G., Bleeker, A., Grennfelt, P., van Grinsven, H., Grizzetti, B., Eds.; Cambridge University Press: Cambridge, UK, 2011; pp. 1–8.
2. Allan, J.D. Landscapes and Riverscapes: The Influence of Land Use on Stream Ecosystems. *Ann. Rev. Ecol. Evol. Syst.* **2004**, *35*, 257–284. [[CrossRef](#)]
3. Billen, G.; Garnier, J.; Lassaletta, L. The nitrogen cascade from agricultural soils to the sea: Modelling nitrogen transfers at regional watershed and global scales. *Phil. Trans. R. Soc. B* **2013**, *368*, 20130123. [[CrossRef](#)] [[PubMed](#)]
4. Butterbach-Bahl, K.; Gundersen, P.; Ambus, P.; Augustin, J.; Beier, C.; Boeckx, P.; Kitzler, B. Nitrogen Processes in Terrestrial Ecosystems. In *The European Nitrogen Assessment: Sources, Effects and Policy Perspectives*; Sutton, M., Howard, C., Erisman, J.W., Billen, G., Bleeker, A., Grennfelt, P., van Grinsven, H., Grizzetti, B., Eds.; Cambridge University Press: Cambridge, UK, 2011; pp. 99–125.
5. Erisman, J.W.; Galloway, J.N.; Seitzinger, S.; Bleeker, A.; Dise, N.B.; Roxana Petrescu, A.M.; Leach, A.M.; Vries, W. Consequences of human modification of the global nitrogen cycle. *Phil. Trans. R. Soc. B* **2013**, *368*. [[CrossRef](#)] [[PubMed](#)]
6. Kyllmar, K.; Stjernman Forsberg, L.; Andersson, S.; Mårtensson, K. Small agricultural monitoring catchments in Sweden representing environmental impact. *Agric. Ecosyst. Environ.* **2014**, *198*, 25–35. [[CrossRef](#)]
7. Hatano, R.; Nagumo, T.; Kuramochi, K. Impact of nitrogen cycling on stream water quality in a basin associated with forest, grassland, and animal husbandry, Hokkaido, Japan. *Ecol. Eng.* **2005**, *24*, 509–515. [[CrossRef](#)]
8. Garnier, M.; Recanatesi, F.; Ripa, M.N.; Leone, A. Agricultural nitrate monitoring in a lake basin in central Italy: A further step ahead towards an integrated nutrient management aimed at controlling water pollution. *Environ. Monit. Assess.* **2010**, *170*, 273–286. [[CrossRef](#)] [[PubMed](#)]
9. Bryan, B.A.; Kandulu, J.M. Designing a Policy Mix and Sequence for Mitigating Agricultural Non-Point Source Pollution in a Water Sup Catchment. *Water Resour. Manag.* **2011**, *25*, 875–892. [[CrossRef](#)]
10. Bechmann, M. Nitrogen losses from agriculture in the Baltic Sea region. *Agric. Ecosyst. Environ.* **2014**, *198*, 13–24. [[CrossRef](#)]
11. Jarvis, S.; Hutchings, N.; Brentrup, F.; Olesen, J.; van der Hoek, K. Nitrogen Flows in Farming Systems across Europe. In *The European Nitrogen Assessment: Sources, Effects and Policy Perspectives*; Sutton, M., Howard, C., Erisman, J.W., Billen, G., Bleeker, A., Grennfelt, P., van Grinsven, H., Grizzetti, B., Eds.; Cambridge University Press: Cambridge, UK, 2011; Chapter 10; pp. 211–228.
12. Billen, G.; Garnier, J.; Mouchel, J.-M.; Silvestre, M. The Seine system: Introduction to a multidisciplinary approach of the functioning of a regional river system. *Sci. Total Environ.* **2007**, *375*, 1–2. [[CrossRef](#)] [[PubMed](#)]
13. Billen, G.; Silvestre, M.; Grizzetti, B.; Leip, A.; Garnier, J.; Voss, M.; Howarth, R.; Bouraoui, F.; Lepisto, A.; Kortelainen, P.; et al. Nitrogen Flows from European Regional Watersheds to Coastal Marine Waters. In *The European Nitrogen Assessment: Sources, Effects and Policy Perspectives*; Sutton, M., Howard, C., Erisman, J.W., Billen, G., Bleeker, A., Grennfelt, P., van Grinsven, H., Grizzetti, B., Eds.; Cambridge University Press: Cambridge, UK, 2011; Chapter 13; pp. 271–297.
14. Jiang, R.; Hatano, R.; Zhao, Y.; Woli, K.P.; Kuramochi, K.; Shimizu, M.; Hayakawa, A. Factors controlling nitrogen and dissolved organic carbon exports across timescales in two watersheds with different land uses. *Hydrol. Process.* **2014**, *28*, 5105–5121. [[CrossRef](#)]
15. Oenema, O.; Oudendag, D.; Velthof, G.L. Nutrient losses from manure management in the European Union. *Livest. Sci.* **2007**, *112*, 261–272. [[CrossRef](#)]
16. Aguilera, R.; Marcé, R.; Sabater, S. Detection and attribution of global change effects on river nutrient dynamics in a large Mediterranean basin. *Biogeosciences* **2015**, *12*, 4085–4098. [[CrossRef](#)]
17. Hirt, U.; Kreins, P.; Kuhn, U.; Mahnkopf, J.; Venohr, M.; Wendland, F. Management options to reduce future nitrogen emissions into rivers: A case study of the Weser river basin, Germany. *Agric. Water Manag.* **2012**, *115*, 118–131. [[CrossRef](#)]

18. Deelstra, J.; Iital, A.; Povilaitis, A.; Kyllmar, K.; Greipsland, I.; Blicher-Mathiesen, G.; Lagzdins, A. Reprint of “Hydrological pathways and nitrogen runoff in agricultural dominated catchments in Nordic and Baltic countries”. *Agric. Ecosyst. Environ.* **2014**, *198*, 65–73. [[CrossRef](#)]
19. Lawniczak, A.E.; Zbierska, J.; Nowak, B.; Achtenberg, K.; Grześkowiak, A.; Kanas, K. Impact of agriculture and land use on nitrate contamination in groundwater and running waters in central-west Poland. *Environ. Monit. Assess.* **2016**, *188*, 172. [[CrossRef](#)] [[PubMed](#)]
20. Ding, J.; Jiang, Y.; Fu, L.; Liu, Q.; Peng, Q.; Kang, M. Impacts of land use on surface water quality in a subtropical River Basin: A case study of the Dongjiang River Basin, Southeastern China. *Water* **2015**, *7*, 4427–4445. [[CrossRef](#)]
21. Giri, S.; Qiu, Z.; Prato, T.; Luo, B. An integrated approach for targeting critical source areas to control nonpoint source pollution in watersheds. *Water Resour. Manag.* **2016**, *30*, 5087–5100. [[CrossRef](#)]
22. Blaas, H.; Kroeze, C. Excessive nitrogen and phosphorus in European rivers: 2000–2050. *Ecol. Indic.* **2016**, *67*, 328–337. [[CrossRef](#)]
23. Törnqvist, R.; Jarsjö, J.; Thorslund, J.; Rao, P.S.C.; Basu, N.B.; Destouni, G. Mechanisms of basin-scale nitrogen load reductions under intensified irrigated agriculture. *PLoS ONE* **2015**, *10*, e0120015. [[CrossRef](#)] [[PubMed](#)]
24. Lassaletta, L.; Romero, E.; Billen, G.; Garnier, J.; Garcia-Gomez, H.; Rovira, J.V. Spatialized N budgets in a large agricultural Mediterranean watershed: High loading and low transfer. *Biogeosciences* **2012**, *9*, 57–70. [[CrossRef](#)]
25. Van Rijswijk, M.; Gilissen, H.K.; van Kempen, J. The need for international and regional transboundary cooperation in European river basin management as a result of new approaches in EC water law. *ERA Forum* **2010**, *11*, 129–157. [[CrossRef](#)]
26. Varol, M. Temporal and spatial dynamics of nitrogen and phosphorus in surface water and sediments of a transboundary river located in the semi-arid region of Turkey. *Catena* **2012**, *100*, 1–9. [[CrossRef](#)]
27. Nevado, J.J.B.; Martín-Doimeadios, R.C.R.; Guzmán Bernardo, F.J.; Jiménez Moreno, M.; Ortega Tardío, S.; Sánchez-Herrera Fornieles, M.; Martín-Nieto Rios, S.; Doncel Pérez, A. Integrated pollution evaluation of the Tagus River in Central Spain. *Environ. Monit. Assess.* **2011**, *156*, 461–477. [[CrossRef](#)] [[PubMed](#)]
28. Garrote, L.; Granados, A.; Iglesias, A. Strategies to reduce water stress in Euro-Mediterranean river basins. *Sci. Total Environ.* **2016**, *543*, 997–1009. [[CrossRef](#)] [[PubMed](#)]
29. European Commission. Report from the Commission to the European Parliament and the Council on the Implementation of the Water Framework Directive (WFD) (2000/60/EC)—River Basin Management Plans. 2012. Available online: <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=COM:2012:0670:FIN:EN:PDF> (accessed on 21 December 2016).
30. Martins, G.; Ribeiro, D.; Pacheco, D.; Cruz, J.V.; Cunha, R.; Gonçalves, V.; Nogueira, R.; Brito, A.G. Prospective scenarios for water quality and ecological status in Lake Sete Cidades (Portugal): The integration of mathematical modelling in decision processes. *Appl. Geochem.* **2008**, *23*, 2171–2181. [[CrossRef](#)]
31. Kronvang, B.; Hoffmann, C.C.; Droge, R. Sediment deposition and net phosphorus retention in a hydraulically restored lowland river floodplain in Denmark: Combining field and laboratory experiments. *Mar. Freshw. Res.* **2009**, *60*, 638–646. [[CrossRef](#)]
32. Malagó, A.; Bouraoui, F.; Viggiak, O.; Grizzetti, B.; Pastori, M. Modelling water and nutrient fluxes in the Danube River Basin with SWAT. *Sci. Total Environ.* **2017**, *603–604*, 196–218. [[CrossRef](#)] [[PubMed](#)]
33. Johnes, P.J. Evaluation and management of the impact of land use change on the nitrogen and phosphorus load delivered to surface waters: The export coefficient modelling approach. *J. Hydrol.* **1996**, *183*, 323–349. [[CrossRef](#)]
34. Agência Portuguesa do Ambiente (APA). *Plano de Gestão da Região Hidrográfica do Tejo e Ribeiras do Oeste (RH5), Parte 2—Caracterização e Diagnóstico*; Autoridades Portuguesas: Lisboa, Portugal, 2015; p. 176. (In Portuguese)
35. Confederación Hidrográfica del Tajo (CHT). *Plan Hidrológico de la Parte Española de la Demarcación Hidrográfica del Tajo—Memoria*. *Ministerio de Agricultura, Alimentación y Medio Ambiente*; Gobierno de España: Madrid, Spain, 2015; p. 128. (In Spanish)
36. Kilsby, C.G.; Tellier, S.S.; Fowler, H.J.; Howels, T.R. Hydrological impacts of climate change on the Tejo and Guadiana Rivers. *Hydrol. Earth Syst. Sci. Discuss.* **2007**, *11*, 1175–1189. [[CrossRef](#)]
37. CLC, Corine Land Cover. Version 18.5.1. 2006. Available online: <http://land.copernicus.eu/pan-european/corine-land-cover/clc-2006/view> (accessed on 14 October 2016).

38. López-Moreno, J.I.; Vicente-Serrano, S.M.; Begueria, S.; García-Ruiz, J.M.; Portela, M.M.; Almeida, A.B. Dam effects on droughts magnitude and duration in a transboundary basin: The lower river Tagus, Spain and Portugal. *Water Resour. Res.* **2009**, *45*, W02405. [[CrossRef](#)]
39. Gómez, C.M.; Delacámara, G.; Pérez, C.D.; Ibáñez, E.; Solanes, M. *EPI WATER: Evaluating Economic Policy Instruments for Sustainable Water Management in Europe*; WP3 EX-POST Case Studies: Water Transfers in the Tagus River Basin (Spain), Deliverable no.: D3.1—Review Reports; EPI-WATER: Milan, Italy, 2011.
40. Agência Portuguesa do Ambiente (APA). *Plano de Gestão da Região Hidrográfica do Tejo e Ribeiras do Oeste (RH5), Parte 3—Análise Económica das Utilizações da Água*; Autoridades Portuguesas: Lisboa, Portugal, 2015; p. 179. (In Portuguese)
41. Confederación Hidrográfica del Tajo (CHT). *Plan Hidrológico de la Parte Española de la Demarcación Hidrográfica del Tajo-Anejo 3 de la Memoria: Usos y Demandas de Agua*. Ministério de Agricultura, Alimentación y Medio Ambiente; Gobierno de España: Madrid, Spain, 2015; p. 73. (In Spanish)
42. Confederación Hidrográfica del Tajo (CHT). Ministério de Agricultura, Alimentación y Medio Ambiente, Gobierno de España. 2016. Available online: www.chtajo.es/Informacion%20Ciudadano/Calidad_Vertidos/Resultados_Informes/Documents/AguasSuperficiales/Red%20ICA/Informes_ICA.htm (accessed on 9 January 2017). (In Spanish)
43. SNIRH, Sistema Nacional de Informação de Recursos Hídricos. 2016. Available online: <http://snirh.apambiente.pt/index.php?idMain=> (accessed on 14 December 2016). (In Portuguese)
44. SNIAmb, Sistema Nacional de Informação de Ambiente. 2017. Available online: <https://sniamb.apambiente.pt/content/cat%C3%A1logo?language=pt-pt> (accessed on 21 July 2017). (In Portuguese)
45. GeoPortal, Geographic Portal Information of Spain. 2017. Available online: <http://sig.mapama.es/geoportail/> (accessed on 21 July 2017).
46. Novotny, V.; Olem, H. *Water Quality: Prevention, Identification and Management of Diffuse Pollution*; Van Nostrand Reinhold: New York, NY, USA, 1994; Volume 9, pp. 507–572. ISBN 9780442005597.
47. Instituto Nacional de Estatística (INE). Efectivo Animal (nº) da Exploração Agrícola por Localização Geográfica (NUTS–2002) e Espécie animal. Recenseamento Agrícola—Séries Históricas. 2009. Available online: https://www.ine.pt/xportal/xmain?xpid=INE&xpgid=ine_indicadores&indOcorrCod=0004460&contexto=bd&selTab=tab2 (accessed on 3 July 2017). (In Portuguese)
48. Lau, P.S.; Tam, N.F.Y.; Wong, Y.S. Wastewater nutrients removal by *Chlorella vulgaris*: Optimization through acclimation. *Environ. Technol.* **1996**, *17*, 183–189. [[CrossRef](#)]
49. Tanik, A.; Ozalp, D.; Seker, Z. Practical estimation and distribution of diffuse pollutants arising from watershed in Turkey. *J. Environ. Sci. Technol.* **2013**, *10*, 221–230. [[CrossRef](#)]
50. Cordovil, C.M.; de Varennes, A.; Pinto, R.; Fernandes, R.C. Changes in mineral nitrogen, soil organic matter fractions and microbial community level physiological profiles after application of digested pig slurry and compost from municipal organic wastes to burned soils. *Soil Biol. Biochem.* **2011**, *43*, 845–852. [[CrossRef](#)]
51. Haygarth, P.; Johnes, P.; Butterfield, D. *Land Use for Achieving “Good Ecological Status” of Water Bodies in England and Wales: A Theoretical Exploration for Nitrogen and Phosphorus*; HMSO: London, UK, 2003; 30p.
52. Erturk, A.; Gurel, M.; Ekdal, A.; Tavsan, C.; Seker, D.Z.; Çokgor, E.U.; Insel, G.; Mantas, E.P.; Aydin, E.; Ozgun, H.; et al. Estimating the Impact of Nutrients Emissions via Water Quality Modelling in the Melen Watershed. In Proceedings of the IWA 11th Diffuse Pollution Conference, Chiang, Thailand, 19–22 November 2007; Volume 167, pp. 26–31.
53. Eurostat Statistics Explained. Share of Holdings with Livestock Which Have Manure Storage Facilities in Total Holdings with Livestock by Size of the Holding in Livestock Units, EU-28, IS, NO, CH and ME. 2010. Available online: http://ec.europa.eu/eurostat/statistics-explained/index.php/File:Share_of_holdings_with_livestock_which_have_manure_storage_facilities_in_total_holdings_with_livestock_by_size_of_the_holding_in_livestock_units,_EU-28,_IS,_NO,_CH_and_ME,_2010_.png (accessed on 4 July 2017).
54. European Environment Agency (EEA). Changes in Wastewater Treatment in Southern European Countries between 1980s and 2009. 2013. Available online: <http://www.eea.europa.eu/data-and-maps/figures/changes-in-wastewater-treatment-in-countries-of-europe-between-1980s-and-2005-southern-3> (accessed on 12 December 2016).
55. Agência Portuguesa do Ambiente (APA). *Questões Significativas da Gestão da Água (QSiGA)*; Participação Pública: Lisboa, Portugal, 2014; 138p. (In Portuguese)

56. Instituto Nacional de Estatística (INE). *Estatísticas Agrícolas 2015*; Instituto Nacional de Estatística: Lisboa, Portugal, 2016; pp. 7–60. ISBN 978-989-25-0360-78.
57. Confederación Hidrográfica del Tajo (CHT). *Proposta do Plano Hidrológico do Lado Espanhol da Região Hidrográfica do Tejo, Ciclo de Planificação 2015-2021: Efeitos Ambientais Transfronteiriços Espanha-Portugal*; Ministerio de Agricultura, Alimentación y Medio Ambiente, Gobierno de España: Madrid, España, 2015; p. 26. (In Spanish/Portuguese).
58. Agência Portuguesa do Ambiente (APA). *Plano de Gestão da Região Hidrográfica do Tejo e Ribeiras do Oeste (RH5), Parte 6—Programa de Medidas*; Autoridades Portuguesas: Lisboa, Portugal, 2016; p. 190. (In Portuguese)
59. Christianson, L.; Tyndall, J.; Helmers, M. Financial comparison of seven nitrate reduction strategies for Midwestern agricultural drainage. *Water Resour. Econ.* **2013**, *2–3*, 30–56. [[CrossRef](#)]
60. Brito, A.G.; Maia, R.; Silva, C.; Fernandes, T.; Lacerda, M. The Portuguese-Spanish Cooperation on Transboundary Water Governance: The Way Forward. In Proceedings of the 8th International Conference of the European Water Resources Association (EWRA), Porto, Portugal, 26–29 June 2013.
61. Roebeling, P.; Alves, H.; Rocha, J.; Brito, A.G.; Mamede, J. Gains from trans-boundary water quality management in linked catchment and coastal socio-ecological systems: A case study for the Minho region. *Water Resour. Econ.* **2014**, *8*, 32–42. [[CrossRef](#)]
62. Agência Portuguesa do Ambiente (APA); Direcção-Geral de Agricultura e Desenvolvimento Rural (DGADR). *Poluição Provocada por Nitratos de Origem Agrícola—Directiva 91/676/CEE, de 12 de dezembro. Relatório 2012–2015*; Autoridades Portuguesas: Lisboa, Portugal, 2016; p. 235. (In Portuguese)
63. Confederación Hidrográfica del Tajo (CHT). *Plan Hidrológico de la Parte Española de la Demarcación Hidrográfica del Tajo-Anejo 4 de la Memoria: Registro de Zonas protegidas. Ministério de Agricultura, Alimentación y Medio Ambiente*; Gobierno de España: Madrid, Spain, 2015; p. 563. (In Spanish)
64. European Environment Agency (EAA). Nitrate Vulnerable Zones. 2009. Available online: <http://eea.europa.eu/data-and-maps/figures/nitrate-vulnerable-zones-eu> (accessed on 15 February 2017).
65. Gil, A.M.; Amorós, A.M.R.; Hernández, M.H. El trasvase Tajo-Segura. *Obs. Medioambient.* **2005**, *8*, 73–110.
66. Lorenzo-Lacruz, J.; Vicente-Serrano, S.M.; López-Moreno, J.I.; Beguería, S.; García-Ruiz, J.M.; Cuadrat, J.M. The impact of droughts and water management on various hydrological systems in the headwater of the Tagus River (central Spain). *J. Hydrol.* **2010**, *386*, 13–26. [[CrossRef](#)]
67. Cameira, M.R.; Fernando, R.M.; Ahuja, L.; Pereira, L. Simulating the fate of water in field soil–crop environment. *J. Hydrol.* **2005**, *315*, 1–24. [[CrossRef](#)]
68. Cameira, M.R.; Fernando, R.M.; Ahuja, L.R.; Ma, L. Using RZWQM to simulate the fate of nitrogen in field soil–crop environment in the Mediterranean region. *Agric. Water Manag.* **2007**, *90*, 121–136. [[CrossRef](#)]
69. Cameira, M.R.; Pereira, A.; Ahuja, L.R.; Ma, L. Sustainability and environmental assessment of fertigation in an intensive olive grove under Mediterranean conditions. *Agric. Water Manag.* **2014**, *146*, 346–360. [[CrossRef](#)]
70. Simas, T.C.; Ferreira, J.G. Nutrient enrichment and the role of salt marshes in the Tagus estuary (Portugal). *Estuar. Coast. Shelf Sci.* **2007**, *75*, 393–407. [[CrossRef](#)]
71. Mendes, M.P.; Ribeiro, L. Nitrate probability mapping in the northern aquifer alluvial system of the river Tagus (Portugal) using Disjunctive Kriging. *Sci. Total Environ.* **2010**, *408*, 1021–1034. [[CrossRef](#)] [[PubMed](#)]



Reproduced with permission of copyright owner. Further reproduction prohibited without permission.