

Article

Incorporating In-Stream Nutrient Uptake into River Management: Gipuzkoa Rivers (Basque Country, North Spain) as a Case Study

Maddi Altuna ¹, Eugènia Martí ², Francesc Sabater ³, José Ramón Díez ⁴ , Joan Lluís Riera ³, Félix Izco ⁵ and Arturo Elosegi ^{1,*} 

¹ Department of Plant Biology and Ecology, University of the Basque Country (UPV/EHU), 48940 Leioa, Spain; altuna.maddi@gmail.com

² Center for Advanced Studies of Blanes (CEAB-CSIC), 17300 Blanes, Spain; eugenia@ceab.csic.es

³ Department of Evolutionary Biology, Ecology and Environmental Sciences, University of Barcelona, 08028 Barcelona, Spain; fsabater@ub.es (F.S.); jlriera@ub.edu (J.L.R.)

⁴ Department of Mathematics and Experimental Sciences Education, University of the Basque Country (UPV/EHU), 48940 Leioa, Spain; joseamon.diez@ehu.es

⁵ Province Government of Gipuzkoa, 2004 Donostia-San Sebastián, Spain; fizco2009@hotmail.es

* Correspondence: arturo.elosegi@ehu.es; Tel.: +34-664-391-18

Received: 8 February 2019; Accepted: 6 May 2019; Published: 11 May 2019



Abstract: Gipuzkoa (Basque Country, North Spain) is an industrial region where investments in sanitation and wastewater treatment have improved water quality and partially recovered river biological communities. However, further technological improvements are unlikely. Our objective was to assess whether in-stream self-purification may contribute to improvement of the trophic state of rivers. We propose an integrative approach to assessing river water quality, which diagnoses problems, identifies likely causes and prescribes solutions. We first analysed the loads of nutrients transported by Gipuzkoa rivers and compared them with the potential nutrient uptake rates (estimated from published empirical regressions). In reaches where both of them were within one order of magnitude, we considered that the self-purification capacity of river channels may influence nutrient concentrations. Then, we selected some river reaches where no other water quality problems beyond nutrient concentrations occurred and ran the expert system STREAMES 1.0 to diagnose the problems and detect their causes. The studied reaches differed in their problems and in their potential solutions. We empirically determined nutrient retention in two streams by means of mass balances and slug nutrient additions. We detected large differences in retention capacity between reaches and siltation as one of the main problems affecting the self-purification capacity of the study streams. Finally, we used STREAMES 1.0 to identify potential solutions to specific river sections. The results obtained so far point towards an important potential of in-stream bioreactive capacity to reduce nutrient loads and to specific restoration activities that may improve the functionality and trophic status of the streams in Gipuzkoa.

Keywords: nutrient retention; ammonium; nitrate; phosphate; STREAMES; stream; uptake rate

1. Introduction

Rivers are among the ecosystems most threatened by human activities [1–3], including dam building [4], alteration of flow regimes [5], water abstraction [6], pollution [7], channel modification [8] and climate change [9]. These threats also affect the sustainability of human activities, since rivers provide ecosystem services that are essential to society [10,11] and thus, complex programmes have been devised to monitor, assess and restore the health of river ecosystems [12].

Nutrients and organic matter pollution still cause main concerns in rivers [13,14], as well as in nearby coastal zones [15]. Excess concentration of nutrients and organic matter, caused by agricultural, urban or industrial activities, results in eutrophication of water ecosystems [16], a process whose side effects include proliferation of noxious algae, anoxia, fish kills or foul taste and smell [17]. Furthermore, eutrophication of freshwaters causes large economic costs in terms of water purification [18], environmental costs [19], as well as health costs, as eutrophic waters often harbour pathogens [20] and can directly harm human health by excess nutrient concentration [21]. Large efforts have been made in many parts of the world to reduce or revert the problems caused by nutrients in freshwaters [22]. The most common management approaches focus on the source of nutrients and include measures to reduce nutrient loading, such as improved sewage systems [23], advanced wastewater treatment plants (WWTP) [18] and improving fertilization practices in agricultural fields [24]. Despite these efforts, nutrient problems are still common in freshwaters [22] and significant reductions in nutrient inputs often involve expensive technologies, such as tertiary wastewater treatment, with reduced benefits [18].

Much less emphasis has been placed on managing the receiving water bodies to reduce nutrient problems, despite the fact that river ecosystems are characterized by their active biogeochemical capacity [25]. This capacity is affected by multiple human pressures, among which those affecting hydraulics, sediment characteristics or redox potential stand out [26,27]. One key element is the hyporheic zone, the portion of sediments that is permeated with stream water, where the combination of long retention times, strong redox gradients and diverse microbial metabolism provide the opportunity to modify water chemistry during propagation through river networks [28,29]. Hydraulic conductivity across the hyporheic zone can be reduced by siltation and by modifications in channel form [30], what has led to projects aiming at restoring hydraulic conductivity as a means to reduce nutrient concentration [31,32]. Similarly, changes in channel geometry, in riparian shading or in connectivity between channel and floodplain can reduce nutrient retention and have thus been addressed by restoration projects [33–36]. Although the effect of nutrient uptake on downstream transport depends on the subsequent fate of the nutrient, as uptake may be balanced by mineralization, it may alter the timing of transport through fluctuations in storage or, in the case of denitrification, may remove nutrients permanently [37]. Whatever the case, the focus on in-stream processes for river management has seldom been applied to entire river networks [33]. Nutrient abatement strategies by river managers could benefit greatly from taking into account the capacity of river channels to retain, store and process nutrients.

In this paper, we present a diagnosis of nutrient status in rivers in Gipuzkoa, one of the most densely populated and industrial provinces in Spain. Our aim was to provide water managers with information on in-stream nutrient uptake to complement current management strategies, which have so far had a limited success regarding nutrient status, as a consequence of the constraints imposed by intensive human pressure. For this purpose, we combined a range of approaches, from surveys to field experimentation and the use of an expert system to assess nutrient uptake and identify potential alternatives to further reduce nutrient concentrations.

2. Study Site

Gipuzkoa (Basque Country, North Spain) is a mountainous and highly populated region where over 700,000 inhabitants live in only 1909 km², mostly concentrated in industrial towns along river margins (Figure 1). The climate is temperate oceanic, with rainfall over 1500 mm y⁻¹ regularly distributed throughout the year. The landscape is dominated by fast-growing tree plantations, rough pastures in mountaintops, meadows in mid to low altitudes and by industrial and urban areas. The main industrial sectors are iron and steel metallurgy, equipment goods, machine-tool industry, rubber and plastics and paper and cardboard industry [38]. As a result of all these activities, rivers in Gipuzkoa have a long history of pollution, which peaked in the second half of the 20th century and has since decreased steadily as a result of improved industrial processes, improved sanitation and wastewater treatment [39]. This improvement has also had dramatic effects on riverine communities and ecosystem functioning [40]. Nevertheless, in 2009, 57% of the water bodies still did not achieve the good ecological

status or potential [41], 25% were below good chemical quality (<http://www4.gipuzkoa.net>) and 40% showed benthic chlorophyll concentrations typical of mesotrophic to eutrophic conditions [42]. It must be noted that the main concern of local managers is on nutrient concentration, not on nutrient loads, as rivers are short and drain directly to the open ocean, where processes such as internal recycling are of minor concern [43]. Therefore, even if a large fraction of the nutrient load is transported by rivers during floods [44], when instream processes are less important [45,46], nutrient transformations during baseflow would still make a difference from the point of view of managers. Nutrient uptake has been shown to be an important factor for self-purification in the Agüera Stream [47], which is located in the nearby province of Biscay and is similar to rivers from Gipuzkoa. There, intense growth of algal biofilm results in strong assimilatory nutrient uptake during baseflows, whereas storms scour algal mats thus resetting the stream to a highly retentive system [48]. Therefore, we consider assimilatory nutrient retention to make an important contribution to the reduction of nutrient concentration during baseflow periods, that is, during the periods in which non-compliance with environmental standards is most common [49].

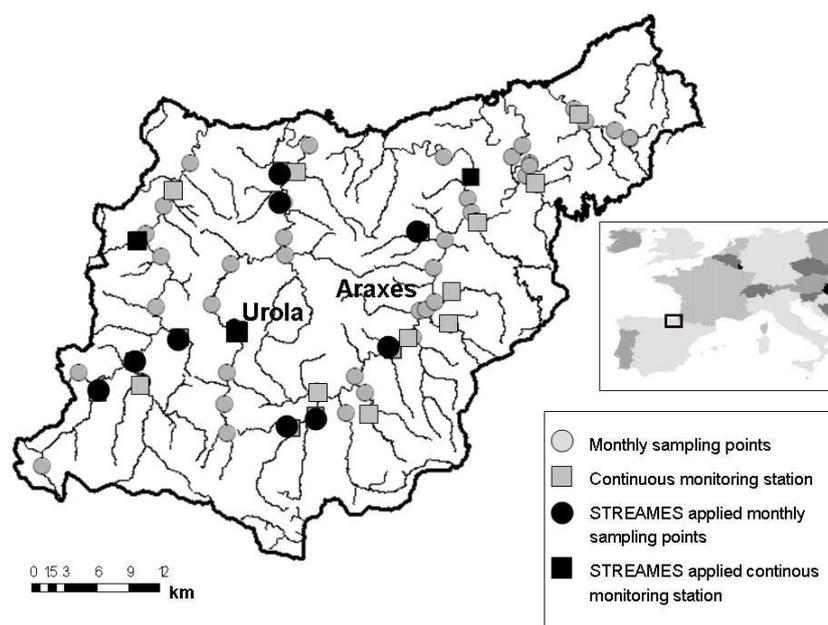


Figure 1. The river network of Gipuzkoa. Circles represent the 64 monthly sampling sites, squares are the 13 continuous monitoring stations operated by the Province Government. Highlighted in black are the sections where STREAMES 1.0 was applied. Araxes and Urola, sections where we carried out empirical nutrient retention experiments.

3. Materials and Methods

To assess the nutrient status of rivers in Gipuzkoa we used data collected by the water agencies, from which we calculated nutrient loads and estimated potential nutrient uptake (see below). Based on this information, we grouped river sections into three categories: (a) sections with no nutrient problems (i.e., nutrient concentrations complied with regulations), (b) sections with moderate problems (i.e., where in-stream processes had the potential to influence nutrient status) and (c) sections with severe problems (i.e., nutrient fluxes were well above the in-stream nutrient uptake). In sections with moderate problems we used the STREAMES 1.0 Environmental Decision Support System (see below) to diagnose reach-level problems associated with nutrients, identify their potential causes and suggest solutions.

Based on the most common causes of impairment detected by the expert system, we performed direct field measurements of nutrient uptake at selected sections to empirically test how these causes affected nutrient retention. Finally, we combined all this information to provide managers with a show card of management actions at different spatial scales, from catchment to reach, that can be selected according to site-specific constraints.

3.1. Measurement of Nutrient Loads and Potential Nutrient Uptake

The loads of ammonium, nitrate and phosphate (in mg s^{-1}) transported by rivers were calculated for the hydrological year 2008–2009 from data on discharge and nutrient concentrations measured at 77 stream sites monitored by the Province Government of Gipuzkoa (Figure 1). Thirteen of these sites were continuously monitored and 64 sites were sampled monthly. At continuously monitored points data on discharge and water quality were recorded every 10 min. Nutrient load there was calculated multiplying concentration by discharge and the average used to estimate load for the hydrological year 2008–2009. At sites that were sampled monthly, we estimated the discharge in the moment of sampling by correcting the discharge in the nearest continuous gauging station in the same drainage basin by the ratio of drainage area in the gauging site to the drainage area in the monthly sampling site. Then, load was calculated multiplying the concentration of each nutrient (measured colorimetrically by the Province Government in its main laboratory) by the estimated discharge. The annual load was calculated as the average of monthly instant loads.

We estimated the potential nutrient uptake rate (U , $\text{mg s}^{-1} \text{m}^{-2}$) expected in our rivers if they were in pristine status. This estimation was based on the assumption that nutrient uptake efficiency is governed by discharge [25,37] and is highest in pristine rivers [50]. U was calculated following Equation (1).

$$U = C \cdot Q / S_w \cdot w \quad (1)$$

where C is ambient nutrient concentration (mg L^{-1}), Q is annual average discharge (L s^{-1}), w is average width at each site (m) and S_w is potential nutrient uptake length (m). Values of S_w , an estimate of nutrient uptake efficiency, were inferred at each site from Q following published regressions [37,51,52] reported for pristine rivers. For this estimate of potential nutrient uptake in pristine conditions, ambient nutrient concentration was set as the average concentration at the site with lowest nutrient levels in Gipuzkoa ($39 \mu\text{g L}^{-1} \text{N-NH}_4^+$, $280 \mu\text{g L}^{-1} \text{N-NO}_3^-$ and $16 \mu\text{g L}^{-1} \text{P-PO}_4^{3-}$). As mentioned above, potential nutrient uptake in Gipuzkoa is likely driven by assimilatory uptake by the algal biofilm. This process results in a temporary removal of nutrients, as these will be released later when algal biomass decays [53]. Nevertheless, frequent rain events under the oceanic climate occurring in Gipuzkoa scour most algal biomass [48] and thus, assimilatory uptake results in an effective reduction of nutrient concentration during baseflow periods.

We calculated the ratio between nutrient load and potential nutrient uptake rate to estimate the potential importance of in-stream processes in controlling nutrient dynamics at the scale of river sections (ca. km-long). For this purpose, nutrient loads were expressed in units of $\text{mg s}^{-1} \text{m}^{-2}$ by dividing average annual load by the areal surface of 1-km stream sections (i.e., section length by wetted width).

3.2. Diagnose and Potential Causes of Nutrient Impairment

We selected 11 sections (Figure 1) where the ratio of nutrient load to potential nutrient uptake were in the same order of magnitude (load/uptake ratio < 10), which suggests that in-stream nutrient uptake there has a potential to influence nutrient concentrations. In these sections we applied STREAMES 1.0, an expert system that can be freely downloaded from <http://www.streames.net/>, to diagnose section-level problems associated with nutrients, identify their potential causes and suggest solutions. STREAMES 1.0, an improved version from that described in Reference [54], is a computer application that supports the decision-making processes in stream reach management by encompassing heuristic (expert) and empirical information. It can be used to infer the river state related to functionality features (i.e., the self-purification capacity of the stream), to diagnose the problems affecting a particular stream reach, to suggest potential causes for each of the detected problems and to propose a list of suitable management actions to each problem diagnosed, taking into account their potential causes. To accomplish this, STREAMES makes use of a knowledge base that includes, in the form of decision trees, the heuristic knowledge provided by scientists and managers to diagnose problems and detect causes, as well as a database of stream management actions cross-linked with problem categories and potential causes.

For each section, STREAMES 1.0 requires information on hydrology and water quality, channel morphology, in-stream habitat, riparian vegetation and catchment characteristics including presence of point-source inputs. Data on discharge and water quality (pH and electric conductivity, concentrations of oxygen, ammonium, nitrate and soluble reactive phosphorus, turbidity and total suspended solids, biological and chemical oxygen demands) were provided by the Province Government. Catchment characteristics (area of the drainage basin, lithology and soil uses) were calculated with ArcView 9.3 on the digital maps of the Province Government (<https://b5m.gipuzkoa.eus/>). The presence of free-ranging livestock and of gravel extraction was checked with the managers and rangers from the Province Government. The rest of the information needed to run STREAMES was collected in visual inspections of 100–500 m reaches upstream from each point. Therefore, we assessed the structure of riparian vegetation, the abundance of modifications of river channel and banks, the dominant type of substrate, the proportion of riverbed covered by fine sediments, the presence of filamentous green algae, macrophytes, as well as sewage fungus. Finally, the Province Government provided information on biological indicators based on algae, invertebrate and fish.

3.3. Empirical Measurements of Nutrient Uptake

Outputs from STREAMES suggested a set of potential causes of nutrient impairment, some of which occurred in many of the study sections. We performed field experiments in 2 sections (Figure 1) to gain additional information on actual in-stream nutrient uptake and factors controlling it.

One section is located in the middle part of Urola River (Figure 1) and is 12-km long. It is affected by the effluent from a WWTP located 1.5 km upstream from the head of the section. Along the section there is also a quarry that is a source of silt-sized sediments, a small neighbourhood (Aizpurutxo) and 2 hydropower plants that divert part of the discharge and revert it several kilometres downstream. We sampled the section on 4 occasions from June to September 2010, collecting samples at 11 points along the section, at the inflow of all tributaries and at all the outflows (2 water diversion canals and the main stream). At each sampling site we measured discharge (FP101 Global Water current meter), temperature and conductivity (WTW) and took water samples, which were filtered (Whatman GF/F), carried to the laboratory in a cold box and analysed for nitrate, ammonia and soluble reactive phosphorus colorimetrically [55]. The load of nutrients at each point was calculated by multiplying concentration times discharge and a global mass-balance between all inputs and outputs was calculated, which allowed estimating the percentage of net nutrient uptake at the section scale (i.e., $\text{output-input}/\text{input}$). Negative percentages indicate net uptake of nutrients along the section, while positive percentages indicate net release.

Additionally, in the same section we examined the effects of the silt inputs from the Urola quarry on nutrient uptake by comparing reaches immediately upstream (control reach) and downstream (impacted reach) from the silt inputs. Nutrient uptake was assessed following the slug addition method [56]. We added 30 L of a solution containing NH_4Cl and $\text{Na}(\text{H}_2\text{PO}_4)\cdot\text{H}_2\text{O}$ as nutrient sources and NaCl as a hydrologic tracer [57] in a single pulse at the head of the reach. We recorded conductivity at the downstream end of the reach every 5 s from the beginning of the addition pulse until conductivity returned to pre-addition values (conductivity meter WTW 330). Water samples were collected in 250 mL acid-washed plastic bottles every 10–60 s at the bottom of the reach over the conductivity-pulse passage. Samples were filtered (Whatman GF/F), stored on ice, transported to the laboratory and frozen until analysis. We calculated nutrient uptake length (S_w , m), following a mass balance between mass of nutrient added and mass of nutrient retrieved based on nutrient concentrations measured at the bottom of the reach [58]. Additionally, at these reaches, we also measured the biomass and chlorophyll-*a* of periphyton, which is likely the biotic component most involved in nutrient uptake in this section. Cobbles (6 per reach) were collected and scraped, the slurry was filtered through two Whatman GF/F filters and carried to the lab on ice. One filter was used to determine the ash-free dry mass (AFDM) by drying it at 105 °C for 24 h and ashing it at 500 °C for 4 h. The second filter was stored frozen in the laboratory until analysis of chlorophyll-*a* following [59]. The results of nutrient

and biofilm metrics were log-transformed for normality and significance of differences between control (upstream from the silt inputs) and impact (downstream) reaches was analysed by means of a *t*-test.

Empirical measurements of nutrient uptake were also performed in the Araxes Stream (Figure 1) to assess the response of in-stream nutrient uptake to an increase in channel morphological complexity. We compared a reach where logs had been introduced into the channel to restore the physical habitat for trout with an unrestored reach located upstream. At each reach, we performed slug additions of ammonium and phosphate (as described above) on 3 dates during August 2013.

3.4. Management Proposals

Finally, we used STREAMES 1.0 to produce a set of management proposals for abatement of nutrient problems, which are based on the combination of problems and causes identified at the study sections. From the large set of potential management actions provided by STREAMES we selected the most suitable based on our own experience and on discussions with stakeholders from water agencies and environmental managers.

4. Results

4.1. Nutrient Loads and Potential Nutrient Uptake

The loads of dissolved inorganic nutrients transported by Gipuzkoa streams ranged from 0.1 to 450 Mg N y⁻¹ for ammonium, from 7.5 to 4806 Mg N y⁻¹ for nitrate and 0.1 to 157 Mg P y⁻¹ for phosphate. These values correspond to 1×10^{-5} –0.71 mg N s⁻¹ m⁻² for ammonium, 0.08×4.5 mg N s⁻¹ m⁻² for nitrate and 7×10^{-4} –0.14 mg P s⁻¹ m⁻² for phosphate, respectively. Potential uptake rates, estimated from literature relationships, ranged between 0.004 and 0.016 (mg N s⁻¹ m⁻²) for ammonium, 0.072 and 1.25 (mg N s⁻¹ m⁻²) for nitrate and 0.002 and 0.009 (mg P s⁻¹ m⁻²) for phosphate. Therefore, the ratio between loads and potential uptake rates ranged from 0.03 to 141 for ammonium (median = 3.7), from 0.06 to 39.3 for nitrate (median = 3.2) and from 0.12 to 53.4 for phosphate (median = 6.3). Based on this ratio, the potential uptake in Gipuzkoa rivers is within an order of magnitude of the nutrient load (Figure 2). In 15–23% of the studied sections the potential nutrient uptake is higher or similar to the nutrient load, which suggests some potential to improve nutrient status based on in-stream nutrient processing. This represents 11 of the studied sections. In general, ratios higher than 10 were found in the main courses (Figure 2), indicating a smaller possibility of improving the situation by means of in-stream processes.

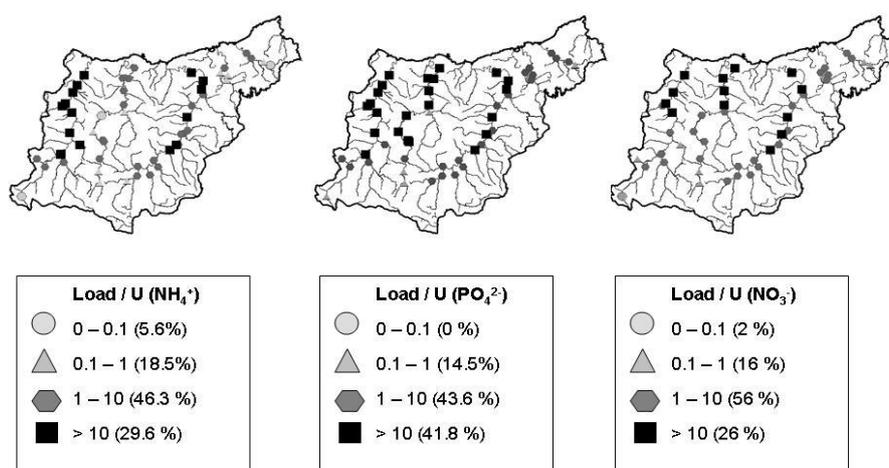


Figure 2. Ratios between nutrient loads and potential uptake rates (both expressed in mg s⁻¹ m⁻²) at each section studied for ammonium, phosphate and nitrate. In parenthesis, percentage of sections in each category range.

4.2. Diagnoses and Potential Causes of Nutrient Impairment

For the 11 sections selected, STREAMES 1.0 suggested the most common problems were clogging of the riverbed (i.e., siltation of the interstices between bed particles) and high phosphate and ammonium loading. In addition, loading of nitrate was a problem in 6 sections, loading of organic matter in 5 and low oxygenation in 3 (Table 1). STREAMES 1.0 outputs also pointed to a low in-stream self-purification capacity and a low buffering capacity of the riparian vegetation. In all studied sections, alteration of the riparian vegetation was considered as one of the main causes of nutrient problems, often combined with riverbed alteration. In addition, in almost all sections, point-source inputs were identified as a cause of nutrient impairment. Only 3 sections seemed to be affected by industrial pollution and 2 by WWTP effluents. Finally, in one section the main affection seemed to be related to dairy activities.

Table 1. Diagnosis of nutrient problems and detection of causes based on STREAMES 1.0 simulations.

Diagnosis		Causes	
Clogging		Riparian vegetation alteration	100%
Severe	18%		
Moderate	36%	Riverbed alteration	64%
Slight	27%		
	82%	Point-source inputs	82%
PO₄³⁻ loading			
Severe	45%	WWTP	18%
Moderate	36%		
	82%	Industrial pollution	27%
NH₄⁺ loading			
Severe	36%	Stabled livestock	9%
Moderate	27%		
Slight	36%		
	100%		
NO₃⁻ loading			
Severe	18%		
Moderate	36%		
	55%		
OM loading			
Severe	45%		
	45%		
Hypoxia			
Moderate	27%		
	27%		
Self-purification capacity			
Low	45%		
Moderate	36%		
High	18%		
Riparian buffer capacity			
Low	82%		
Moderate	9%		
High	9%		

4.3. Empirical Measurements of Nutrient Uptake

Mass balances along the Urola section showed water outflow to be higher than the sum of detected inflows in the 4 sampling campaigns (Table 2), with the difference decreasing with decreasing discharge as the summer progressed. Hydropower derivation canals leaked water as diverted discharge was consistently higher than the amount reverted below the turbine. The leaks accounted for 46% of water diverted in June and decreased to 10% in September. The net balance between inputs and outputs for nitrate was positive on all dates (Table 2), net release along the section representing 1% to 106% of the total nitrate inputs. On the other hand, the balance between ammonium outputs and inputs was always negative (Table 2), with net uptake along the reach accounting for 27–100% of inputs. Finally, the balance between inputs and outputs for phosphate shifted from being positive in June and July (i.e., net uptake) to negative in August and September (i.e., net release).

Table 2. Global mass balance results from June, July, August and September 2010 samplings in Urola Stream. b.d.l.: below detection level.

	2 June				6 July				18 August				16 September			
	Q	N-NO ₃ ⁻	N-NH ₄ ⁺	P-PO ₄ ³⁻	Q	N-NO ₃ ⁻	N-NH ₄ ⁺	P-PO ₄ ³⁻	Q	N-NO ₃ ⁻	N-NH ₄ ⁺	P-PO ₄ ³⁻	Q	N-NO ₃ ⁻	N-NH ₄ ⁺	P-PO ₄ ³⁻
	L s ⁻¹	mg s ⁻¹	mg s ⁻¹	mg s ⁻¹	L s ⁻¹	mg s ⁻¹	mg s ⁻¹	mg s ⁻¹	L s ⁻¹	mg s ⁻¹	mg s ⁻¹	mg s ⁻¹	L s ⁻¹	mg s ⁻¹	mg s ⁻¹	mg s ⁻¹
Input C1	366	844	60	37	404	1016	13	57	146	479	4	10	141	639	13	32
∑ tributaries	166	199	3	4	229	276	1	5	135	201	16	7	61	102	2	1
Quarry spill	4	7	1	b.d.l	0	0	0	0	3	4	b.d.l	b.d.l	0	0	0	0
∑ hydroelectric release	267	690	2	13	356	516	b.d.l	20	132	318	3	4	99	445	2	9
∑ INPUTS	802	1741	65	53	989	1808	14	82	415	1003	23	20	301	1186	17	43
∑ hydroelectric capture	496	1879	3	33	503	1003	b.d.l	41	146	358	3	4	109	490	3	11
Output C10	582	1711	25	49	756	1180	b.d.l	47	357	659	12	8	259	781	10	16
∑ OUTPUTS	1078	3590	28	82	1259	2183	b.d.l	88	503	1017	15	11	368	1272	13	27
Outputs-Inputs	275	1849	-38	29	270	375	-14	6	88	14	-9	-8	67	86	-5	-16
% Out-inp/∑ inputs	34	106	-58	55	27	21	-100	7	21	1	-37	-42	22	7	-27	-37
% Out-inp/∑ inputs	34	106	-58	55	27	21	-100	7	21	1	-37	-42	22	7	-27	-37

At a smaller spatial scale, results from nutrient addition experiments showed uptake lengths in the reach receiving the Urola quarry inputs longer than those in the control reach (Table 3). This difference was larger for phosphate than for ammonium uptake lengths. In addition, periphyton biomass was significantly higher (t -test, $p < 0.05$) in the control ($51.2 \pm 6.9 \text{ g m}^{-2}$) than in the impacted reach ($24.4 \pm 1.9 \text{ g m}^{-2}$). Periphyton chlorophyll-*a* was also significantly higher (t -test, $p < 0.05$) in the control ($61.8 \pm 12.1 \text{ mg m}^{-2}$) than in the impacted reach ($13.1 \pm 2.6 \text{ mg m}^{-2}$).

Table 3. Ammonium and phosphate uptake lengths (S_w , m) measured in September 2013 at reaches located upstream and downstream from the Urola quarry inputs. Longer nutrient uptake lengths indicate lower nutrient uptake efficiencies.

	$S_w\text{-NH}_4^+$ (m)		$S_w\text{-PO}_4^{-3}$ (m)	
	4 September	5 September	4 September	5 September
Upstream reach (control)	111	201	327	377
Downstream reach (impacted)	117	283	1929	580

In the Araxes Stream, ammonium uptake lengths were consistently longer at the control than at the restored reach on all sampling dates (average $S_w\text{-control}:S_w\text{-restored} = 1.6$; Table 4). Uptake lengths for phosphate were also longer at the control reach, the difference being larger than for ammonium (average $S_w\text{-control}:S_w\text{-restored} = 2.6$).

Table 4. Ammonium and phosphate uptake lengths (S_w , m) measured in August 2013 at a control and a restored reach in the Araxes Stream.

	$S_w\text{-NH}_4^+$ (m)			$S_w\text{-PO}_4^{-3}$ (m)		
	8 August	12 August	13 August	8 August	12 August	13 August
Control reach	323	570	612	239	275	580
Restored reach	283	293	339	118	117	167

4.4. Management Actions Proposed by STREAMES

STREAMES 1.0 offered a battery of management proposals for abatement of nutrient loads, of which the 23 most suitable are listed in Table 5. Among these proposals, 11 addressed catchment-scale actions. Improved connection of sanitation networks was proposed for 10 of the 11 the study sections. Proposals at catchment scale also include optimization of existing WWTP, nutrient management in agricultural areas and enhancement of environmental flows. At the river channel scale STREAMES provided 7 proposals. The most common proposals were re-creation of natural riparian vegetation and re-profiling of channel banks. Four additional proposals focussed on the alluvial zone and the streambed, being the plantation of macrophytes the most common (4 sections).

Table 5. List of actions selected among those proposed by STREAMES 1.0, indicating the number of stream sections where these actions were suitable.

Actions	No. Sections
<i>Catchment</i>	
1. Complete sanitation connection	10
2. Best management practices (BMPs) in agriculture/livestock	1
3. Nutrient management plan in agriculture	1
4. Ecological flow maintenance	3
5. Best Available industrial Techniques (BAT)	3
6. Reduction or elimination of weirs	1
7. Biological filter (construction of a new WWTP)	1
8. Planted systems (plant soil treatment by irrigating with residual waters)	2
9. Optimization of the denitrification treatment (WWTP improvement)	1
10. Optimize WWTP phosphorus removal treatment	2
11. Optimize solids removal process (WWTP improvement)	1

Table 5. Cont.

Actions	No. Sections
<i>River channel</i>	
12. Reprofile channel banks	5
13. Installation of live current deflectors	4
14. Boulder clusters emplacement	1
15. Re-creation of natural vegetation on channel banks	7
16. Using vegetation to restore stream sinuosity	2
17. Willow mattress revetment	1
18. Willow spilling	2
19. Vegetated gabions	3
<i>Alluvial zone</i>	
20. Buffer strips	1
21. Channel by-pass to ensure the inundation of the adjacent floodplain	1
<i>Streambed</i>	
22. Creation of in-channel pools	1
23. Planting macrophytic vegetation	4

5. Discussion

In this study, we propose an integrative approach to assess water quality associated with river networks, which diagnoses problems, identifies the likely causes and prescribes potential solutions for nutrient status. In addition, this approach was applied to a remarkable number of river sections (77), which covered a large range of nutrient concentrations reflecting the wide diversity of environmental pressures in the drainage basins of the region [43].

A unique aspect of our approach is that it explicitly considers the in-stream bioreactive capacity (i.e., nutrient uptake) as a relevant aspect in both the diagnosis and prescription evaluation steps. Existing literature has shown that the bioreactive capacity of streams and rivers can greatly reduce the overall loads of nutrients exported from catchments [25,60] and thus, it is considered as a relevant ecosystem service [36,61,62]. Human pressures such as high nutrient loads [50,63] or alterations of channel morphology [64] negatively affect this in-stream capacity, potentially resulting in higher nutrient exports. Conversely, recent studies point at river restoration as a good strategy to mitigate water nutrient problems because it can increase in-stream nutrient uptake [33,35]. In this context, in order to use this bioreactive capacity as part of the diagnosis and prognosis of water quality problems it is important not only to assess the nutrient uptake of a given stream under its current environmental conditions but also to predict its potential nutrient uptake assuming conditions under lack of pressures. According to the literature, nutrient uptake length (an indicator of nutrient uptake efficiency) increases with discharge [37,51,52], especially in pristine rivers where nutrient uptake is highest [50]. In this sense, we used existing regressions between discharge and nutrient uptake length from a compiled dataset as a predictive model to estimate potential nutrient uptake of the selected sections. We compared this potential uptake to stream nutrient fluxes to assess the relative importance of in-stream processes in regulating nutrient fluxes. Where uptake and fluxes were within the same order of magnitude, we considered that there was scope for the improvement of nutrient status based on actions to promote in-stream bioreactivity. This criterion (e.g., potential uptake similar to flux) must be taken as a rough rule-of-thumb. Of course, nutrient uptake also varies greatly with discharge, season and other factors that we did not consider. But whenever uptake rate is close to flux, there is scope to improve the nutrient status based on promoting uptake rate, what would at least reduce nutrient concentration during baseflows and thus improve river chemical status during the periods when non-compliance with regulations are most frequent.

We are aware that uptake values from nutrient addition experiments (used in our case to calculate potential nutrient uptake) express gross rates, which can be counterbalanced by release in other reaches or other moments, resulting in no overall decline in nutrient concentrations [53]. Nevertheless, mass-balance studies along nutrient-enriched rivers show strong uptake [65] and it is likely that the effect of in-stream retention on nutrient concentrations will be highest in reaches where potential

retention is close to the transported load. Indeed, gross nutrient uptake from experimental additions has been combined in some cases with net nutrient uptake from reach-scale mass-balances and the results were not too different [58,66], thus suggesting that, in absence of better data, results from one approach can be used to infer trends for the other. Furthermore, as a consequence of the rainy climate and torrential characteristics of rivers in the region, floods scour frequently the benthic biofilm [48], resulting in permanent removal from the river systems of the nutrients stored therein.

Of the 77 sections studied, 57 complied with the WFD nutrient regulations, 13 presented moderate nutrient problems and 7 had severe nutrient problems. The sections with no nutrient problems were in general small mountain tributaries, whereas the nutrient problems were widespread in medium to low reaches of larger streams. Although the latter sections are subject to multiple stressors derived from a high human pressure [43], our findings suggest that in-stream bioreactivity could help to mitigate these problems. Therefore, in these sections management strategies should consider actions addressed to increase in-stream uptake [34], such as restoring channel complexity [67]. Alternatively, in sections with severe problems where nutrient fluxes are orders of magnitude higher than potential uptake capacity, other solutions must be prioritised such as implementation of best management practices in key activities at the basin level (e.g., [68]) or an improvement in the end-of-the-pipe regulation of nutrient sources (enhanced sanitation, advanced WWTP treatments [69]). In any case, the European experience suggests that, although sanitation, wastewater treatment and changes in productive systems can dramatically reduce river pollution, they rarely eliminate all problems [70]; therefore, it is likely that in-stream uptake will have key importance even after implementation of end-of-the-pipe regulations.

In the sections with moderate problems, results from STREAMES identified excess NH_4^+ and PO_4^{3-} loading and riverbed clogging as the main nutrient problems and suggested alteration of riparian vegetation, point-source inputs and riverbed alteration as their most likely causes. Despite large amounts of money spent in the last decades to improve sanitation and wastewater treatment and despite clear improvements in water quality, the nutrient problems still have not disappeared from Gipuzkoa [71], as is also the case of many other regions in Europe and North America [19,72]. There are several reasons for this. First, there are still undetected inputs, as for example, in some towns where the rivers have been buried underground and receive water from an obsolete and frequently leaking sewer system [43]. Second, the effluents from large WWTPs can make a significant contribution to the receiving rivers, whose discharge and thus, dilution capacity, can be severely reduced in dry periods. This is especially the case for the mid and high sections of the Oria, Urola and Deba rivers, where the human population and industrial activities are very intense [73] and baseflow discharge is low. The contribution of WWTP effluents to total discharge in these sections can be as high as 35% and even higher in drought periods [49]. And third, the geomorphological status of rivers in Gipuzkoa is mostly poor as a consequence of the heavy occupation of floodplains and the modification of banks for flood defences [71]. On the other hand, riverbed clogging, caused by deposition of silt on the channel, seems to be a consequence of high erosion rates, associated mainly to forest activities in steep slopes [43,74], as well as to the very common water diversions in the region [43,52], which reduce flow velocity and promote deposition of fine sediments [75]. These problems of nutrients and riverbed clogging are far from being restricted to Gipuzkoa, as they can affect river basins in many urbanised regions of the world [76].

The empirical determination of nutrient retention in different rivers corroborated the low nutrient retention capacity of some of our sections and pinpointed some of the causes. Urola River showed low capacity to retain phosphorus and turned out to be a source, not a sink for DIN. In the case of nitrogen, the fact that the largest imbalance between inputs and outputs occurred in June, at the end of a period with strong rain, suggests that the imbalance corresponds to undetected inputs, which could correspond to some farm or to groundwater [77] and not to instream transformations of organic N, as the mass of organic matter stored in the river bed was lowest during this period. In the case of phosphorus, the comparison of the reaches upstream and downstream from the quarry showed the detrimental effects of siltation on algal growth and on nutrient retention. Fine sediment deposition is a

major disturbance in streams, since it affects algae and invertebrates [78] and seals the hyporheos [79], thereby reducing nutrient retention. Indeed, deposition of fine sediment has been described as a “master stressor” given its pervasive effects on river biota and its intense interactions with other stressors [80]. In the Urola section, the nearby quarry seemed to be the main source of fine sediments but our STREAMES results suggest that riverbed clogging has a prevalent impact in the Basque rivers. Siltation, especially from intensive forest plantations, has been identified as an important impact in the region [43] but the likely consequences for nutrient uptake have not been considered so far by managers. Interestingly enough, our results, albeit based in a single project and a few sampling campaigns, point out at a positive effect of trout habitat restoration on nutrient retention. Similar results in other channel renaturalization projects in Gipuzkoa [81] and elsewhere [82,83] suggest that such projects can have positive effects beyond the fish habitat, which can be considered ecosystem services [61]. This particular restoration project in Araxes Stream consisted on adding large-wood structures forming low jams and deflectors, which together increased flow heterogeneity and created patches of fast flowing water with no deposition of fine sediments.

Whatever the case, the results from empirical nutrient retention experiments agree in general with the diagnose offered by STREAMES 1.0, which suggests that the specific measures offered by the latter hold potential for improving the status of rivers in Gipuzkoa. Overall, STREAMES 1.0 suggested 23 potential actions to improve the nutrient status: 11 actions at catchment level, 8 at channel level, 2 in the alluvial zone and 2 in the streambed. The action with potential benefits in more sites was improved sanitation, followed by recreation of natural bank vegetation, re-profiling riverbanks, installation of current deflectors and planting macrophytic vegetation. STREAMES 1.0 is based on information provided by water managers and from published literature and thus, there is reasonable evidence to back the effectiveness of the actions it proposes. But the feasibility and cost-effectiveness of the individual actions must be checked on a site-by-site basis, as the biophysical and societal constraints differ widely across regions. In this sense, improved sanitation is a constant priority of the local managers, as reflected in the revision of the Hydrologic Plans to complain with the WFD [43,71]. Also, although the main network of WWTPs in Gipuzkoa is considered to be already finished, the Province Government, the Basque Water Agency and the public companies operating the WWTPs are constantly monitoring and seeking ways to improve the effectiveness of these facilities, especially nutrient and suspended solid removal. Other actions such as restoring riparian vegetation or reprofiling channel banks are more difficult to implement, given the intense human occupation of riparian areas and floodplains by high density urban and industrial areas in Gipuzkoa. Nevertheless, some opportunities arise, especially linked to the implementation of the EU Habitats Directive, which promotes, among other goals, the restoration of habitats, including aquatic and riparian, and the Floods Directive, which seeks to reduce the damages caused by floods. These objectives are being addressed, among others, by means of projects to improve instream and riparian habitats as well as restore riparian wetlands in Natura 2000 sites, of complete channel re-configuration projects to minimise flood in urban areas [84] or of demolition of dams and weirs to promote river connectivity (e.g., <https://www.irekibai.eu>). Also, the maturity and cover of riparian forests has increased during the last years in many river sections [43] as awareness of managers on the importance of these forests increased. Other actions proposed by STREAMES 1.0, such as planting macrophytes, seem less suited to the steep and torrential rivers in the zone. Whatever the case, the present exercise makes managers aware of potential remedies to current nutrient problems, which will likely result in them seizing more opportunities to improve the status of river ecosystems.

The framework we present here can easily be transferred to other regions with problems of nutrients in rivers, which are frequent around the globe [85]. In particular, we hold that it is important to consider in-stream processes as part of an integral solution to the existing problems. STREAMES 1.0 can help scientists and managers towards this goal.

Author Contributions: Conceptualization, A.E. and E.M., software, M.A., E.M., J.L.R. and F.S., fieldwork, M.A. and A.E., calculations, M.A., resources, A.E., writing, all authors, project administration, A.E., funding acquisition, A.E.

Funding: This research was funded by the Department of Hydraulic Works, Province Government of Gipuzkoa.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses or interpretation of data; in the writing of the manuscript or in the decision to publish the results. F.I. participated as an author after retiring from the Province Government.

References

1. Dudgeon, D.; Arthington, A.H.; Gessner, M.O.; Kawabata, Z.-I.; Knowler, D.J.; Leveque, C.; Naiman, R.J.; Prieur-Richard, A.H.; Soto, D.; Stiassny, M.L.; et al. Freshwater biodiversity: Importance, threats, status and conservation challenges. *Biol. Rev.* **2006**, *81*, 163–182. [[CrossRef](#)] [[PubMed](#)]
2. Vorosmarty, C.J.; McIntyre, P.B.; Gessner, M.O.; Dudgeon, D.; Prusevich, A.; Green, P.; Glidden, S.; Bunn, S.E.; Sullivan, C.A.; Liermann, C.R.; et al. Global threats to human water security and river biodiversity. *Nature* **2010**, *467*, 555–561. [[CrossRef](#)] [[PubMed](#)]
3. Sabater, S.; Elozegi, A.; Ludwig, R. *Multiple Stressors in River Ecosystems: Status, Impacts and Prospects for the Future*; Elsevier: Amsterdam, The Netherlands, 2019.
4. Nilsson, C.; Reidy, C.A.; Dynesius, M.; Revenga, C. Fragmentation and flow regulation of the world's large river systems. *Science* **2005**, *308*, 405–408. [[CrossRef](#)] [[PubMed](#)]
5. Poff, N.L.; Zimmerman, J.K.H. Ecological responses to altered flow regimes: A literature review to inform the science and management of environmental flows. *Freshw. Biol.* **2010**, *55*, 194–205. [[CrossRef](#)]
6. Sabater, S. Alterations of the global water cycle and their effects on river structure, function and services. *Freshw. Rev.* **2008**, *1*, 75–88. [[CrossRef](#)]
7. UNEP. *Global Environmental Outlook 4*; Environment for Development: Valletta, Malta, 2007.
8. Gregory, K.J. The human role in changing river channels. *Geomorphology* **2000**, *79*, 172–191. [[CrossRef](#)]
9. Milly, P.C.D.; Dunne, K.A.; Vecchia, A.V. Global pattern of trends in streamflow and water availability in a changing climate. *Nature* **2005**, *438*, 347–350. [[CrossRef](#)]
10. Costanza, R.; d'Arge, R.; de Groot, R.; Farber, S.; Grasso, M.; Hannon, B.; Limburg, K.; Naeem, S.; O'Neill, R.V.; Paruelo, J.; et al. The value of the world's ecosystem services and natural capital. *Nature* **1997**, *387*, 253–260. [[CrossRef](#)]
11. MEA. *Ecosystems and Human Well-Being*; Synthesis: Washington, DC, USA, 2005.
12. Hering, D.; Borja, A.; Carstensen, J.; Carvalho, L.; Elliott, M.; Feld, C.K.; Heiskanen, A.S.; Johnson, R.K.; Moe, J.; Pont, D.; et al. The European water framework directive at the age of 10: A critical review of the achievements with recommendations for the future. *Sci. Total Environ.* **2010**, *408*, 4007–4019. [[CrossRef](#)]
13. Sutton, M.A.; Oenema, O.; Erisman, J.W.; Leip, A.; van Grinsven, H.; Winiwarter, W. Too much of a good thing. *Nature* **2011**, *472*, 159–161. [[CrossRef](#)] [[PubMed](#)]
14. Foley, J.A.; DeFries, R.; Asner, G.P.; Barford, C.; Bonan, G.; Carpenter, S.R.; Chapin, F.S.; Coe, M.T.; Daily, G.C.; Gibbs, H.K.; et al. Global consequences of land use. *Science* **2005**, *309*, 570–574. [[CrossRef](#)] [[PubMed](#)]
15. Seitzinger, S.P.; Mayorga, E.; Bouwman, A.F.; Kroeze, C.; Beusen, A.H.W.; Billen, G.; van Drecht, G.; Dumont, E.L.; Fekete, B.M.; Garnier, J.; et al. Global river nutrient export: A scenario analysis of past and future trends. *Glob. Biogeochem. Cycles* **2010**, *24*. [[CrossRef](#)]
16. Smith, V.H. Eutrophication of freshwater and coastal marine ecosystems—A global problem. *Environ. Sci. Pollut. Res.* **2003**, *10*, 126–139. [[CrossRef](#)]
17. Suplee, M.W.; Watson, V.; Teply, M.; McKee, H. How green is too green? Public opinion of what constitutes undesirable algae levels in streams. *J. Am. Water Resour. Assoc.* **2009**, *45*, 123–140. [[CrossRef](#)]
18. Grant, S.B.; Saphores, J.-D.; Feldman, D.L.; Hamilton, A.J.; Fletcher, T.D.; Cook, P.L.M.; Stewardson, M.; Sanders, B.F.; Levin, L.A.; Ambrose, R.F.; et al. Taking the “Waste” Out of “Wastewater” for human water security and ecosystem sustainability. *Science* **2012**, *337*, 681–686. [[CrossRef](#)] [[PubMed](#)]
19. Dodds, W.K.; Bouska, W.W.; Eitzmann, J.L.; Pilger, T.J.; Pitts, K.L.; Riley, A.J.; Schloesser, J.T.; Thornbrugh, D.J. Eutrophication of US freshwaters: Analysis of potential economic damages. *Environ. Sci. Technol.* **2009**, *43*, 12–19. [[CrossRef](#)]
20. Smith, V.H.; Schindler, D.W. Eutrophication science: Where do we go from here? *Trends Ecol. Evol.* **2009**, *24*, 201–207. [[CrossRef](#)]

21. Townsend, A.R.; Howarth, R.W.; Bazzaz, F.A.; Booth, M.S.; Cleveland, C.C.; Collinge, S.K.; Dobson, A.P.; Epstein, P.R.; Holland, E.A.; Keeney, D.R.; et al. Human health effects of a changing global nitrogen cycle. *Front. Ecol. Environ.* **2003**, *1*, 240–246. [[CrossRef](#)]
22. EEA. *European Waters—Current Status and Future Challenges—Synthesis*; EEA Report No 9/2012; EEA: Copenhagen, Denmark, 2012.
23. Walsh, C.J.; Fletcher, T.D.; Ladson, A.R. Stream restoration in urban catchments through redesigning stormwater systems: Looking to the catchment to save the stream. *J. North Am. Benthol. Soc.* **2005**, *24*, 690–705. [[CrossRef](#)]
24. Sharpley, A.; Foy, B.; Withers, P. Practical and innovative measures for the control of agricultural phosphorus losses to water: An overview. *J. Environ. Qual.* **2000**, *29*, 1–9. [[CrossRef](#)]
25. Peterson, B.J.; Wollheim, W.M.; Mulholland, P.J.; Webster, J.R.; Meyer, J.L.; Tank, J.L.; Grimm, N.B.; Bowden, R.D.; Vallet, H.M.; Hershey, A.E.; et al. Control of nitrogen export from watersheds by headwater streams. *Science* **2001**, *292*, 86–90. [[CrossRef](#)] [[PubMed](#)]
26. Krause, S.; Lewandowski, J.; Grimm, N.B.; Hannah, D.M.; Pinay, G.; McDonald, K.; Martí, E.; Argerich, A.; Laurent, P.; Klauset, J.; et al. Ecohydrological interfaces as hot spots of ecosystem processes. *Water Resour. Res.* **2017**, *53*, 6359–6376. [[CrossRef](#)]
27. Pinay, G.; Peiffer, S.; De Dreuzy, J.; Krause, S.; Hannah, D.M.; Fleckenstein, J.H.; Sebilo, M.; Bishop, K.; Hubert-Moy, L. Upscaling nitrogen removal capacity from local hotspots to low stream orders' drainage basins. *Ecosystems* **2015**, *18*, 1101–1120. [[CrossRef](#)]
28. Boano, F.; Harvey, J.W.; Marion, A.; Packman, A.I.; Revelli, R.; Ridolfi, L.; Wörman, A. Hyporheic flow and transport processes: Mechanisms, models, and biogeochemical implications. *Rev Geophys.* **2014**, *43*, 603–679. [[CrossRef](#)]
29. Rode, M.; Hartwig, M.; Wagenschein, D.; Kebede, T.; Borchardt, D. The importance of hyporheic zone processes on ecological functioning and solute transport of streams and rivers. In *Ecosystem Services and River Basin Ecohydrology*; Chicharo, L., Müller, F., Fohrer, N., Eds.; Springer: Berlin, Germany, 2015; pp. 57–82.
30. Naganna, S.R.; Deka, P.C.; Ch, S.; Hansen, W.F. Factors influencing streambed hydraulic conductivity and their implications on stream–aquifer interaction: A conceptual review. *Environ. Sci. Pollut. Res.* **2017**, *24*, 24765–24789. [[CrossRef](#)]
31. Mendoza-Lera, C.; Detry, T. Relating hydraulic conductivity and hyporheic zone biogeochemical processing to conserve and restore river ecosystem services. *Sci. Total Environ.* **2017**, *579*, 1815–1821. [[CrossRef](#)]
32. Merrill, L.; Tonjes, D.J. A review of the hyporheic zone, stream restoration, and means to enhance denitrification. *Crit. Rev. Environ. Sci. Technol.* **2014**, *44*, 2337–2379. [[CrossRef](#)]
33. Newcomer Johnson, T.A.; Kaushal, S.S.; Mayer, P.M.; Smith, R.M.; Svirichi, G.M. Nutrient retention in restored streams and rivers: A global review and synthesis. *Water* **2016**, *8*, 116. [[CrossRef](#)]
34. Craig, L.S.; Palmer, M.A.; Richardson, D.C.; Filoso, S.; Bernhardt, E.S.; Bledsoe, B.P. Stream restoration strategies for reducing river nitrogen loads. *Front. Ecol. Environ.* **2008**, *6*, 529–538. [[CrossRef](#)]
35. Filoso, S.; Palmer, M.A. Assessing stream restoration effectiveness at reducing nitrogen export to downstream waters. *Ecol Appl.* **2011**, *21*, 1989–2006. [[CrossRef](#)]
36. Palmer, M.A.; Filoso, S.; Fanelli, R.M. From ecosystems to ecosystem services: Stream restoration as ecological engineering. *Ecol. Eng.* **2014**, *65*, 62–70. [[CrossRef](#)]
37. Hall, R.O.; Baker, M.A.; Rosi-Marshall, E.J.; Tank, J.L.; Newbold, J.D. Solute-specific scaling of inorganic nitrogen and phosphorus uptake in streams. *Biogeosciences* **2013**, *10*, 7323–7331. [[CrossRef](#)]
38. BG. *Índice de Producción Industrial de la C.A. de Euskadi por MES y Año Según Territorio Histórico*; Official Statistics (included in the Basque Statistics Plan and/or Annual Statistical Program); Basque Government: Vitoria, Spain, 2017.
39. URA. *Proyecto de Plan Hidrológico (PPH) de la Demarcación Hidrográfica Cantábrico Oriental*; BOE-A-2013-6078; URA, the Basque Water Agency: Vitoria, Spain, 2012.
40. Arroita, M.; Elozegi, A.; Hall, R. Twenty years of daily metabolism show riverine recovery following sewage abatement. *Limnol. Oceanogr.* **2019**, *64*, S77–S92. [[CrossRef](#)]
41. URA. *Red de Seguimiento del Estado Biológico de los Ríos*; Informe de Resultados, Campaña 2009; URA, the Basque Water Agency: Vitoria, Spain, 2010.

42. Dodds, W.K.; Jones, J.R.; Welch, E.B. Suggested classification of stream trophic state: Distributions of temperate stream types by chlorophyll, total nitrogen, and phosphorus. *Water Res.* **1998**, *32*, 1455–1462. [[CrossRef](#)]
43. CHC. *Plan Hidrológico de la parte española de la Demarcación Hidrográfica del Cantábrico Oriental*; Documentos Iniciales; CHC: Oviedo, Spain, 2018. Available online: <https://www.chcantabrico.es/planes-hidrologicos-2021-2027/dhc-oriental/documentos-iniciales> (accessed on 11 May 2019).
44. Johnes, P.J. Uncertainties in annual riverine phosphorus load estimation: Impact of load estimation methodology, sampling frequency, baseflow index and catchment population density. *J. Hydrol.* **2007**, *332*, 241–258. [[CrossRef](#)]
45. Drummond, J.D.; Bernal, S.; von Schiller, D.; Martí, E. Linking in-stream nutrient uptake to hydrologic retention in two headwater streams. *Freshw. Sci.* **2016**, *35*, 1176–1188. [[CrossRef](#)]
46. Mainstone, C.P.; Parr, W. Phosphorus in rivers—ecology and management. *Sci. Total Environ.* **2002**, *282*, 25–47. [[CrossRef](#)]
47. Elosegui, A.; Arana, X.; Basaguren, A.; Pozo, J. Self-purification processes along a medium-sized stream. *Environ. Manag.* **1995**, *19*, 931–939. [[CrossRef](#)]
48. Izagirre, O.; Elosegui, A. Environmental control of seasonal and inter-annual variations of periphytic biomass in a North Iberian stream. *Ann. Limnol.* **2005**, *41*, 35–46. [[CrossRef](#)]
49. PGG. *Estudio de la Calidad Biológica de los Ríos de Gipuzkoa*; Province Government of Gipuzkoa: San Sebastian, Spain, 2015.
50. Newbold, J.D.; Bott, T.L.; Kaplan, L.A.; Dow, C.L.; Jackson, J.K.; Aufdenkampe, A.K.; Martin, L.A.; Van Horn, D.J.; de Long, A.A. Uptake of nutrients and organic C in streams in New York City drinking-water-supply watersheds. *J. North Am. Benthol. Soc.* **2006**, *25*, 998–1017. [[CrossRef](#)]
51. Tank, J.L.; Rosi-Marshall, E.J.; Baker, M.A. Are rivers just bigstreams? Using a pulse method to measure nitrogen demand in a large river. *Ecology* **2008**, *89*, 2935–2945. [[CrossRef](#)] [[PubMed](#)]
52. Izagirre, O.; Argerich, A.; Martí, E.; Elosegui, A. Nutrient uptake in a stream affected by hydropower plants: Comparison between stream channels and diversion canals. *Hydrobiologia* **2013**, *712*, 105–116. [[CrossRef](#)]
53. Von Schiller, D.; Bernal, S.; Sabater, F.; Martí, E. A round-trip ticket: The importance of release processes for in-stream nutrient spiraling. *Freshw. Sci.* **2015**, *34*, 20–30. [[CrossRef](#)]
54. Comas, J.; Llorens, E.; Martí, E.; Puig, M.A.; Riera, J.L.; Sabater, F.; Poch, M. Knowledge acquisition in the STREAMES project: The key process in the Environmental Decision Support System development. *AI Commun.* **2003**, *16*, 253–265.
55. APHA. *Standard Methods for the Examination of Water and Wastewater*, 20th ed.; American Public Health Association: Washington, DC, USA, 1998.
56. Wilcock, R.J.; Scarsbrook, M.R.; Costley, K.J.; Nagels, J.W. Controlled release experiments to determine the effects of shade and plants on nutrient retention in a lowland stream. *Hydrobiologia* **2002**, *485*, 153–162. [[CrossRef](#)]
57. Bencala, K.E.; McKnight, D.M.; Zellweger, G.W. Evaluation of natural tracers in an acidic and metal-rich stream. *Water Resour. Res.* **1987**, *23*, 827–836. [[CrossRef](#)]
58. Merseburger, G.; Martí, E.; Sabater, F.; Ortiz, J.D. Point-source effects on N and P uptake in a forested and an agricultural Mediterranean streams. *Sci. Total Environ.* **2011**, *409*, 957–967. [[CrossRef](#)]
59. Jeffrey, S.W.; Humphrey, G.F. New spectrophotometric equations for determining chlorophylls a, b, c1 and c2 in higher plants, algae and natural phytoplankton. *Biochem. Physiol. Pflanz.* **1975**, *167*, 191–194. [[CrossRef](#)]
60. Galloway, J.N.; Dentener, F.J.; Capone, D.G.; Boyer, E.W.; Howarth, R.W.; Seitzinger, S.P.; Asner, C.C.; Cleveland, P.A.; Green, E.A.; Holland, D.M.; et al. Nitrogen cycles: Past, present, and future. *Biogeochemistry* **2004**, *70*, 153–226. [[CrossRef](#)]
61. Acuña, V.; Diez, J.R.; Flores, L.; Meleason, M.; Elosegui, A. Does it make economic sense to restore rivers for their ecosystem services? *J. Appl. Ecol.* **2013**, *50*, 988–997. [[CrossRef](#)]
62. Withers, P.J.A.; Jarvie, H.P. Delivery and cycling of phosphorus in rivers: A review. *Sci. Total Environ.* **2008**, *400*, 379–395. [[CrossRef](#)] [[PubMed](#)]
63. Martí, E.; Aumatell, J.; Gode, L.; Poch, M.; Sabater, F. Nutrient retention efficiency in streams receiving inputs from wastewater treatment plants. *J. Environ. Qual.* **2004**, *33*, 285–293. [[CrossRef](#)] [[PubMed](#)]

64. Sweeney, B.W.; Bott, T.L.; Jackson, J.K.; Kaplan, L.A.; Newbold, J.D.; Standley, L.J.; Hession, W.C.; Horwitz, R.J. Riparian deforestation, stream narrowing, and loss of stream ecosystem services. *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 14132–14137. [[CrossRef](#)] [[PubMed](#)]
65. Martí, E.; Riera, J.L.; Sabater, F. Effects of wastewater treatment plants on stream nutrient dynamics under water scarcity conditions. In *Water Scarcity in the Mediterranean: Perspectives Under Global Change*; Sabater, S., Barceló, D., Eds.; Springer: Berlin, Heidelberg, 2010; pp. 173–195. [[CrossRef](#)]
66. Merseburger, G.C.; Martí, E.; Sabater, F. Net changes in nutrient concentrations below a point source input in two streams draining catchments with contrasting land uses. *Sci. Total Environ.* **2005**, *347*, 217–229. [[CrossRef](#)]
67. Roberts, B.J.; Mulholland, P.J.; Houser, A.N. Effects of upland disturbance and instream restoration on hydrodynamics and ammonium uptake in headwater streams. *J. North Am. Benthol. Soc.* **2007**, *26*, 38–53. [[CrossRef](#)]
68. Teshager, A.D.; Gassman, P.W.; Secchi, S.; Schoof, J.T. Simulation of targeted pollutant-mitigation-strategies to reduce nitrate and sediment hotspots in agricultural watershed. *Sci. Total Environ.* **2017**, *607–608*, 1188–1200. [[CrossRef](#)]
69. Irvine, K.N.; Perrelli, M.F.; McCorkhill, G.; Caruso, J. Sampling and modeling approaches to assess water quality impacts of combined sewer overflows—The importance of a watershed perspective. *J. Great Lakes Res.* **2005**, *31*, 105–115. [[CrossRef](#)]
70. Schinegger, R.; Trautwein, C.; Melcher, A.; Schmutz, S. Multiple human pressures and their spatial patterns in European running waters. *Water Environ. J.* **2012**, *26*, 261–273. [[CrossRef](#)]
71. SG. Real Decreto 1/2016, de 8 de enero, por el que se aprueba la revisión de los Planes Hidrológicos de las demarcaciones hidrográficas del Cantábrico Occidental, Guadalquivir, Ceuta, Melilla, Segura y Júcar, y de la parte española de las demarcaciones hidrog. *Spain Off. J. Span. Gov.* **2016**, *54*, 52–54.
72. Sutton, M.; Howard, C.; Erisman, J.; Billen, G.; Bleeker, A.; Greenfelt, P.; van Grinsven, H.; Grizzetti, B. *The European Nitrogen Assessment. Sources, Effects and Policy Perspectives*; Cambridge University Press: Cambridge, UK, 2011.
73. PGG. *Bases para la Elaboración de las Directrices Sobre el uso Sostenible del Agua en Gipuzkoa*; Province Government of Gipuzkoa: San Sebastian, Spain, 2006.
74. Edeso, J.M.; Merino, A.; Gonzalez, M.J.; Marauri, P. Soil erosion under different harvesting managements in steep forestlands from northern Spain. *L. Degrad. Dev.* **1999**, *10*, 79–88. [[CrossRef](#)]
75. Arroita, M.; Flores, L.; Larrañaga, A.; Martinez, A.; Martínez-Santos, M.; Pereda, O.; Ruiz-Romera, E.; Solagaistua, L.; Elosegi, A. Water abstraction impacts stream ecosystem functioning via wetted-channel contraction. *Freshw. Biol.* **2016**, *62*, 243–257. [[CrossRef](#)]
76. Booth, D.B.; Roy, A.H.; Smith, B.; Capps, K.A. Global perspectives on the urban stream syndrome. *Freshw. Sci.* **2016**, *35*, 412–420. [[CrossRef](#)]
77. Zuo, R.; Chen, X.; Li, X.; Shan, D.; Yang, J.; Wang, J.; Teng, J. Distribution, genesis, and pollution risk of ammonium nitrogen in groundwater in an arid loess plain, northwestern China. *Environ. Earth Sci.* **2017**, *76*, 629. [[CrossRef](#)]
78. Piggott, J.J.; Townsend, C.R.; Matthaei, C.D. Climate warming and agricultural stressors interact to determine stream macroinvertebrate community dynamics. *Glob. Chang. Biol.* **2015**, *21*, 1887–1906. [[CrossRef](#)] [[PubMed](#)]
79. Wood, P.J.; Armitage, P.D. Biological effects of fine sediment in the lotic environment. *Environ. Manag.* **1997**, *21*, 203–217. [[CrossRef](#)]
80. Scarsbrook, M.; McIntosh, A.; Wilcock, B.; Matthaei, C. Effects of agriculture on water quality. In *Advances in New Zealand Freshwater Science*; Jellyman, T.J.A., Davie, C.P., Pearson, J.S.H., Eds.; New Zealand Freshwater Sciences Society & New Zealand Hydrological Society: Thordnon, New Zeland, 2015; pp. 1–22.
81. Elosegi, A.; Elorriaga, C.; Flores, L.; Martí, E.; Díez, J. Restoration of wood loading has mixed effects on water, nutrient, and leaf retention in Basque mountain streams. *Freshw. Sci.* **2016**, *35*, 41–54. [[CrossRef](#)]
82. Bukaveckas, P.A. Effects of channel restoration on water velocity, transient storage, and nutrient uptake in a channelized stream. *Environ. Sci. Technol.* **2007**, *41*, 1570–1576. [[CrossRef](#)]
83. Elosegi, A.; Sabater, S. Effects of hydromorphological impacts on river ecosystem functioning: A review and suggestions for assessing ecological impacts. *Hydrobiologia* **2013**, *712*, 129–143. [[CrossRef](#)]

84. URA. *Informe Para la Comisión Interinstitucional Para la Prevención de Inundaciones en la Cuenca del Río Urumea*; URA, the Basque Water Agency: Vitoria, Spain, 2015.
85. Dodds, W.K.; Smith, V.H. Nitrogen, phosphorus, and eutrophication in streams. *Inl. Waters* **2016**, *6*, 155–164. [[CrossRef](#)]



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).