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Different Approaches to Assessing Pollution Load: The Case of Nitrogen-Related Grey Water Footprint of Barley and Soybean in Argentina

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Abstract: Agriculture is among the main causes of water pollution. Currently, 75% of global anthropogenic nitrogen (N) loads come from leaching/runoff from cropland. The grey water footprint (GWF) is an indicator of water resource pollution, which allows for the evaluation and monitoring of pollutant loads (L) that can affect water. However, in the literature, there are different approaches to estimating L and thus contrasting GWF estimates: (A1) leaching/runoff fraction approach, (A2) surplus approach and (A3) soil nitrogen balance approach. This study compares these approaches for the first time to assess which one is best adapted to real crop production conditions and optimises GWF calculation. The three approaches are applied to assess N-related GWF in barley and soybean. For barley in 2019, A3 estimated a GWF value 285 to 196% higher than A1, while in 2020, the A3 estimate was 135 to 81% higher. Soybean did not produce a GWF due to the crop characteristics. A3 incorporated N partitioning within the agroecosystem and considered different N inputs beyond fertilization, improving the accuracy of L and GWF estimation. Providing robust GWF results to decision-makers may help to prevent or reduce the impacts of activities that threaten the world's water ecosystems and supply.

Keywords: pollution load; nitrogen fertilization; mineralization; leaching/runoff; agricultural practices

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1. Introduction

Currently, agricultural activity is responsible for 70% of global freshwater consumption and represents an important factor in pollution of the resource [1–3]. In order to improve agricultural productivity and meet the food demand, there has been increased dependence on the use of pesticides, fertilisers and manure to address the major productive limitations [3,4]. The use of these compounds has allowed the expansion of agriculture. However, they can generate negative environmental externalities, such as water contamination, when they are used inappropriately, affecting natural ecosystems and human health and livelihoods [1,5,6]. In the case of nitrogen fertilisers, 75% of global anthropogenic nitrogen (N) loads come from leaching/runoff from cropland [1,7,8]. In particular, cereal production and oil crops contribute 18% and 11%, respectively, to the global grey water footprint (GWF) associated with N use [7].

The grey water footprint is defined as the volume of freshwater that is required to assimilate a load of pollutants (L) into a freshwater body, based on natural background concentrations (Cnat) and existing ambient water quality standards (Cmax). GWF is an indicator of the water pollution by an activity that specifies how much of the assimilation capacity of a water body has already been reached [9,10]. Therefore, it is a valid indicator for assessing the impact of some agricultural practices on water resources.

The GWF methodology has evolved over the last 15 years with the use of different L calculation approaches. According to the literature, there are three main approaches for L estimation.

The first approach estimates L as a product between the applied fertiliser rate and the leachate/runoff fraction (α), which represents the fraction of chemicals that can be mobilised to water bodies [10–15]. In this leaching/runoff fraction approach (A1-a), L is assumed as the proportion of chemicals applied to the soil that reaches surface or groundwater bodies [10]. Due to the non-availability of data, studies using this approach consider a constant value of $\alpha = 10$ for different regions and crops, i.e., 10% of the applied fertiliser is lost through leaching/runoff.

In the second approach, L is estimated by applying the α leaching/runoff fraction approach (A1-b) or by using the surplus approach with a β leaching/runoff fraction (A2), where β represents the fraction that can leach or run off from the N surplus left in the soil after harvest [9,16–20]. In both approaches, the fractions are estimated using the climatic, edaphic and agricultural management characteristics of the study area.

The third approach employs an integrative method of L estimation based on the N-balance, which considers the N partitioning within the plant–soil–atmosphere system [7]. The N balance approach (A3) takes into account the complex N dynamics within natural and productive systems, considering the most relevant N inputs and outputs during crop development. This consideration can allow for a more detailed L calculation.

Other studies have estimated the GWF in crops at a global scale, applying a resolution of 10,000 m [7,12,13,18,21]. However, this scale does not allow spatial variations in agrochemical application rates, soil types, management practices and yields to be captured [22,23]. In consequence, the homogenisation of variables results in equally homogeneous L and GWF values, which may not be representative [16,24]. It also does not allow differentiation of the GWF in surface and groundwater [25].

The diversity of approaches and scales implies contrasting and hardly comparable GWF values. It is crucial to have a common calculation of L that can be representative of the reality observed in the field and can be replicated in different regions. However, a comparison between the different approaches used to estimate L has not been addressed yet. This unification of calculations will allow the generation of comparable GWF estimates. On the other hand, the sum of these studies using local scales of analysis would allow for regional estimates that reflect local variations.

Argentina is among the countries with basins that present a high level of water pollution due to anthropogenic N loads [7], with urea being the main N fertiliser applied [26]. Agriculture is a strategic sector in the national economy. It contributes approximately 10% of the gross domestic product and more than 59% of the total value of exports; in addition, it indirectly generates 2 out of 10 private jobs [27]. Argentina is the third largest exporter of soybean and the fourth largest exporter of barley in the world. Approximately 70% of soybean production and 90% of barley production is centred in the Argentine Pampas Region (APR) [28]. Due to the magnitude and international interest of both productions, it is necessary to calculate the volume of GWF associated with N and to know its potential contribution to water resource degradation in order to act accordingly. Thus far, only Tozzini et al. [23] have estimated the soybean GWF associated with N in the northern part of the APR, and there are no studies on barley GWF at a regional or national level.

The aim of this paper is to identify the most accurate method currently available to estimate the N-related GWF. With this purpose, the paper analyses the three main approaches to estimating pollutant loads by applying them to the case of barley and soybean production in Argentina: (1) leaching/runoff fraction approach, (2) surplus approach and (3) nitrogen balance approach. The study highlights the relevance of using an N balance approach with local data for an accurate estimation of L and, consequently, GWF. Using an appropriate L measurement will be helpful to improve the comparability of GWF estimates, and ultimately to understand and prevent the impact of agricultural production on the water environment.

2. Materials and Methods

2.1. Study Area

The study was carried out at barley and soybean plots located in Tandil County, Buenos Aires province, in the southeast of the Argentine Pampas Region (APR) (Figure 1). The climate is humid–sub-humid with a mean annual temperature of approximately 19 °C [29]. The mean annual precipitation is around 800 mm, mainly abundant during the autumn and winter months and with occasional water deficits in summer [30–32]. Typic Argiudoll, characterized by its dark colour, which is strongly developed, well drained and with slopes that do not exceed 3%, is the main type of soil. Furthermore, in some profiles there is a calcium horizon [33].

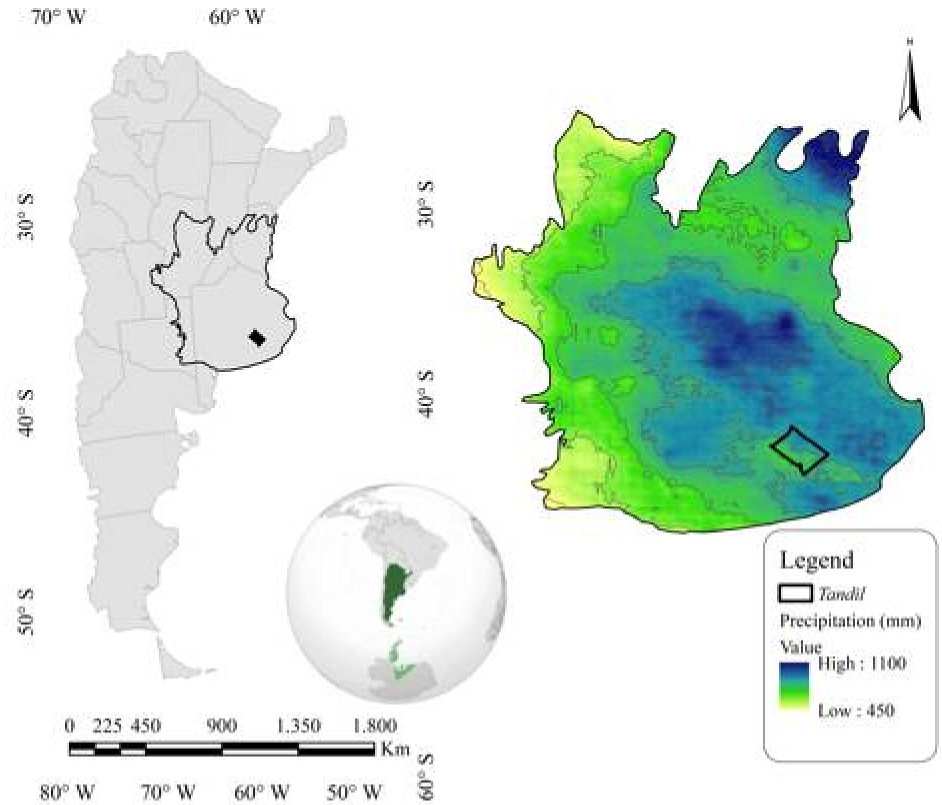

Figure 1. Location of Argentina in South America and location of Argentine Pampas (**left**); location of Tandil County in southeast Pampas Region and distribution of mean annual precipitation within the region (**right**).

Agricultural and livestock activities are well developed in the region. The main crops are produced under rainfed conditions, with wheat and barley growing in winter–spring seasons and soybean, sunflower and maize growing in spring–summer seasons [28,34]. In the last two decades, there has been an expansion and intensification of agricultural activity due to the global demand for agricultural products [34–36]. Argentina exports 60% of the barley produced and around 70% of the soy, with the APR accounting for 70% of soy production and 90% of barley production at the national level [28,37]. This translates into high pressure on the productive and natural systems of the region [35,37,38]. In view of the national and international importance of this region in terms of production and the significant growth of agricultural activity, it is important to have baseline values of L and

GWF that allow the generation of strategies and alternatives in order to provide projections of more sustainable future scenarios.

In this study, barley and soybean crops were monitored and cultivated with the usual agricultural practices in the region.

1. Two growing periods of rainfed malting barley (*Hordeum vulgare* L.) were analysed: in 2019, a plot of 101 ha (37°29′ S, 59°54′ W, 197 m.a.s.l.) where sunflower was previously produced, and in 2020, a plot of 73 ha (37°9′ S, 58°54′ W, 196 m.a.s.l.) where soybean was previously produced. The sowing and harvest dates were 5 July 5 to 17 December 2019 and 7 July to 9 December 2020, respectively. The malting barley was cultivated by applying direct sowing, with row spacing of 0.17 m and a density of 250 seeds per m^2. It was fertilized with urea (46% N), with 220 kg/ha applied the first year and 250 kg/ha the second year.
2. In 2020, a rainfed soybean (*Glycine max* L.) crop of 122 ha (37°30′ S, 58°54′ W, 181 m.a.s.l.) was followed where the predecessor crop was potato. The growing period was from 17 November 2020 to harvest on 5 May 2021. Direct sowing was also applied for this crop, with row spacing of 0.32 m and a density of 35 seeds per m^2. Soybean was fertilized with 180 kg/ha superphosphate (0-21-0).

2.2. Methods

The grey water footprint (GWF, m^3/t) of barley and soybean was assessed using three different approaches in the 2019/2020 and 2020/2021 campaigns, following the methodology proposed by Hoekstra et al. [10].

GWF was calculated as the pollutant load (L, kg/y) divided by the difference between the ambient water quality standard (maximum acceptable concentration (Cmax, kg/m^3)) and the natural concentration in the receiving water body in pristine condition, before significate disturbances (Cnat, kg/m^3). Then, this value was divided by the crop yield (Y, t/ha) (Equation (1)):

$$\mathrm{GWF} = \left[\frac{\mathrm{L}/(\mathrm{C}_{\mathrm{max}} - \mathrm{C}_{\mathrm{nat}})}{\mathrm{Y}}\right] \tag{1}$$

In this study, Cmax for groundwater was assumed to be 0.01 kgN/m^3, the value for drinking water in the Código Alimentario Argentino [39]. This value was used because, in the large plains, the runoff to surface water is negligible and vertical movements (infiltration and evapotranspiration) predominate [40]. A Cnat value of 0.0004 kgN/m^3 was applied in line with the GWF guidelines, as no actual data were available in the study area [7,9]. Y was determined in the field by manual harvest of 0.5 linear meters of each plot of barley and soybean during the physiological maturity stage.

Three approaches were used for estimating L: (1) leaching/runoff fraction [9,10], (2) surplus [9] and (3) nitrogen balance [7].

2.2.1. Estimating the Pollutant Load: Leaching/Runoff Fraction Approach

In this first approach (A1), L was estimated as the product of the N fertilizer application rate in crop production (AR, kgN/ha) and the leaching/runoff fraction (α, dimensionless), defined as the fraction of applied chemicals reaching freshwater bodies (Equation (2)) [9,10]:

$$\mathrm{L} = \alpha \times \mathrm{AR} \tag{2}$$

L was estimated considering two leaching/runoff fractions: A1-a, with α = 10% for N fertilizer, as suggested by Hoekstra et al. [10] and Chapagain et al. [15], in the absence of local data; and A1-b, with α as a function of weather, soil and crop management factors (Equation (3)) [9]:

$$\alpha = \alpha_{\mathrm{min}} + \left[\frac{\sum \mathrm{S_i} \times \mathrm{W_i}}{\sum \mathrm{W_i}}\right] \times (\alpha_{\mathrm{max}} - \alpha_{\mathrm{min}}) \tag{3}$$

where α_{min} and α_{max} are the minimum and maximum N leaching/runoff fraction, respectively, and both values were taken from Table 1 of Franke et al. [9]; and Si is defined as the leaching runoff potential score per factor and is multiplied by the weight of factor Wi, following Franke et al. [9].

2.2.2. Estimating the Pollutant Load: Surplus Approach

In the second approach (A2), L was estimated as the surplus fertiliser [9]. Unlike the previous approach, this is mostly relevant in the case of nutrient application in crops, because it explicitly takes into account the uptake of the chemical substance by plants. Therefore, L is determined by multiplying the leaching/runoff fraction (β, dimensionless) and the N surplus (kgN/ha) after plant uptake and harvest (Equation (4)):

$$L = \beta \times \text{Surplus} \tag{4}$$

where Surplus is calculated as the difference between AR and offtake rate (Offtake, kgN/ha) (Equation (5)):

$$\text{Surplus} = \text{AR} - \text{Offtake} \tag{5}$$

where Offtake is defined as the amount of N taken up by the crop and harvested. Offtake is estimated multiplying Y by the N content in the crop (Nc, kgN/t):

$$\text{Offtake} = Y \times \text{Nc} \tag{6}$$

Nc in malting barley was determined through the protein concentration data reported by the farmer. Protein concentrations of 12.1 and 11.1% in 2019 and 2020, respectively, resulted in Nc of 19.4 and 17.8 kgN/t. Nc was calculated by the Kjeldahl method.

The leaching/runoff fraction β was estimated similarly to α, following the GWF guidelines [9]:

$$\beta = \beta_{min} + \left[\frac{\sum S_i \times W_i}{\sum W_i}\right] \times (\beta_{max} - \beta_{min}) \tag{7}$$

where β_{min} and β_{max} are the minimum and maximum N leaching/runoff fraction, respectively. The two values were taken from Table 2 of Franke et al. [9].

In order to determine α and β as proposed by the GWF guidelines, it was necessary to calculate the environmental factors (annual atmospheric N deposition (AD), soil texture and drainage, mean annual precipitation (Ppm)) and agricultural management factors (AR, Y, N fixation, management practice).

AR and Y were already obtained for the application of Equation (1), while Ppm was taken from Kottek et al. [27], as mentioned in Section 2.1.

AD was calculated with the N-NO_3 concentration in rainwater derived from the hydrological dataset of Zabala et al. [41], which provides data for Del Azul creek basin to the south of the APR. These authors analysed precipitation (Pp) samples (n = 57) during 2010–2019. Subsequently, the average N-NO_3 concentration value was multiplied by the Ppm value.

Soil texture was determined in the laboratory according to the Bouyoucos method [42]. Previously, we took soil samples collected every 10 cm (up to 80 cm depth) before sowing. The soil slope was obtained from GeoINTA [33].

In order to classify the management practices, the questionnaire based on the GWF guidelines in Appendix III [9] was used as a reference.

2.2.3. Estimating the Pollutant Load: Nitrogen Balance Approach

In the third approach (A3), L was estimated by the N balance [7]. The different N inputs and outputs in the agricultural system were determined using Equation (8):

$$\text{N balance} = [N_i + \text{AR} + N_{min} + \text{BNF}] - [\text{offtake} + V + L - R] \tag{8}$$

where N inputs (kgN/ha) are: initial nitrogen concentration available in soil at sowing (N_i), nitrogen fertiliser application rate (AR), nitrogen mineralization (N_{min}) and soybean biological nitrogen fixation (BNF); and N outputs (kgN/ha) are: amount of nitrogen taken up by a crop and harvested (offtake), volatilization of nitrogen fertiliser (V) and nitrogen leaching/runoff (L-R).

N_i was determined by laboratory analysis and provided by the owner of the plots. N_{min} was estimated for the growing season using the model suggested by Reussi Calvo et al. [43] based on anaerobic N (Nan- mg/kg), mean air temperature (T- °C) and Pp (mm) as input variables Equation (9). Nan is an indicator of the potential N-mineralisation of soil and gives the amount of N that can be mineralised. T and water content are environmental factors that regulate the release of N in the soil [43,44].

$$N_{min} = [-252 + 12.3(T) + 1.37(Nan) + 0.27(Pp)] \tag{9}$$

where T and Pp were measured daily at 2 m height by a portable research weather station installed in the plots (sensors CS215-L16 and TE525M Campbell Scientific, Inc., Logan, Utah). Both variables were measured from sowing until the end of the critical crop stage (15 days after anthesis), because that is the time when there is the most important soil mineralization and N absorption from the crop. Nan data were obtained from chemical soil analysis carried out by the farmer. According to [43], the model predicted N_{min} in wheat and maize crops in different sites of the APR (R2 = 0.89, model validation R2 = 0.83).

Soybean, unlike other crops, is a legume that covers its N requirements from the soil input and from BNF [45,46]. BNF was obtained assuming:

$$BNF = [\text{offtake} - (N_i + N_{min})] \tag{10}$$

The V value was obtained through a bibliographic review of studies carried out on crops in the APR, with the same weather, soil and phenological conditions [47,48].

$L - R$ was estimated as a residual term of the N balance, considering $L - R = L$ (Equation (11)):

$$L - R = [(N_i + AR + N_{min}) - (\text{offtake} + V)] \times \beta \tag{11}$$

Atmospheric N deposition was not calculated during the crop growing period, because the study area is mainly used for agricultural activities, in addition to other activities associated with raw material production, such as livestock. There is no industrial development or large urban agglomeration leading to significant N concentrations in the atmosphere.

Denitrification was not included in the N balance, as it occurs when there is high soil-water availability, after events of intense rainfall or in floodplains [47,49,50]. Furthermore, the soils of the study area were well drained [33]. In addition, local studies indicate that denitrification is not an important output, emitting an average of 1.5–2.0% of applied N fertilizer into the atmosphere [47,50].

Finally, the N contained in crop residues was not included in the N balance, because barley and soybean production was carried out with no tillage. This management is based on residue conservation, to protect the soil from erosion and nutrient loss [51].

3. Results

3.1. Estimation of Pollutant Load through the Leaching/Runoff Fraction and Surplus Approach

3.1.1. Estimation of Leaching/Runoff Fractions: α and β

Table 1 presents the environmental factors and agricultural management that were considered for the determination of the leaching and runoff fractions (α and β) in the two crops. The analysed plots were located in the same region. Consequently, the atmospheric, edaphic and weather factors adopted the same values in barley and soybean plots. The soil texture was predominantly loamy with a well-drained profile, and the Ppm was 800 mm. An annual AD value of 0.4 $gN/m^2/y$ was estimated considering an average rainwater concentration of 0.00056 gN/L [41].

Table 1. Estimation of leaching/runoff fractions (α and β) based on environmental factors and agricultural practices specific to analysed plots. Source: Franke et al. [9].

Category	Factor		Leaching-Runoff Potential	Very Low	Low	High	Very High
			Score	**0**	**0.33**	**0.67**	**1**
			Weight α, β				
Environmental Factors	Atmospheric input	N-deposition (AD-gN/m^2/y)	10, 10	x			
	Soil	Texture (relevant for leaching)	15, 15			Loam	
		Texture (relevant for runoff)	10, 10		Loam		
		Natural drainage (relevant for leaching)	15, 15			Well drainage	
		Natural drainage (relevant for runoff)	5, 10		Well drainage		
	Climate	Precipitation (mm/y)	15, 15		600–1200		
Agricultural Practice Factors	Biological N fixation [1] (BNF-kg/ha)		10, 10			35	
	Application rate (AR- kgN/ha)		10, 0			High	
	Plant uptake (crop yield) (Y- t/ha)		5, 0	Very high [2]	High [3]		
	Management practice		10, 15			Average	

[1] Biological N fixation considered only for soybean crop.[2] Plant uptake (crop yield) recorded in barley during 2020.[3] Plant uptake (crop yield) recorded in barley during 2019.

In regards to the agricultural practice factors (Table 1), the BNF in soybean was 35 kgN/ha. The AR for barley was 220 kgN/ha in the first year and 250 kgUrea/ha in the second. Both AR values were considered high, as the average urea rate used for barley during 2019–2020 in the APR was equal to 155 kgUrea/ha [37]. No fertiliser was applied in the soybean plot, therefore its variable was not considered for the α calculation.

In the barley plots analysed, Y was 5.3 t/ha in 2019 and 8.6 t/ha in 2020. The average yield for the country was 3.7 t/ha for barley during 2019–2020 [37]. Specifically, in the centre–southeast of the APR, the yields were from 4.5 to 5.8 t/ha [28]. Comparing these statistics with the Y values obtained in the barley plots, Y was rated as high in 2019 and very high in 2020. In the soybean plot, Y was equal to 3.4 t/ha. This was considered a high value in relation to the average value of 2.8 t/ha reported in Tandil County for the 2019–2020 campaign [28].

The management practice was classified as average, because 6 of the 9 measures listed as good agricultural management practices by the GWF guidelines [9] were employed in the study plots. The measures that were not in line with good practice are as follows:

- There were no diffuse pollution mitigation measures such as buffer zones and stream fencing.
- The handling of chemicals was not careful. In some cases, we observed dumped urea on plot access roads, due to a leak in the transport machinery. The amounts were not significant, but this could be avoided to reduce the potential for fertiliser to move into water bodies.

- No cover crop was used; however, direct seeding and crop rotation were applied in the three crop periods. This management also contributes to soil preservation and prevents water and wind erosion.

Based on Table 1, α values were 0.127, 0.129 and 0.127 for barley in 2019, barley in 2020 and soybean in 2020, respectively. We assumed a rounded α value of 0.13. The α values obtained were consistent with studies carried out on winter crops in the region, which suggests that about 13% of the fertiliser is lost by leaching/runoff [47,52,53].

The β value was calculated similarly to α, as detailed in Table 1. β was 0.42 in barley plots. β was equal to 0.43 in the case of soybean, since the BNF was added as an input variable.

The β value was considerably higher than α, because α represents the fertiliser fraction that can leach or run off, whereas β represents the N surplus fraction that can leach or run off. After harvest, this N surplus in soil can be retained by the soil microflora or lost from the soil–plant system by leaching or runoff. In addition, it can be distributed to the atmosphere by volatilization and denitrification, but in a small proportion [54]. In the southeast of APR, the N losses by volatilization are generally low in winter due to the low temperatures, with losses from 1 to 6% of N-urea added [47,48]. Denitrification is also not a frequent process [47,50], therefore it is possible that 42–43% of the N surplus in the soil can leach or run off and the remaining N will stay in the soil.

3.1.2. Determination of Pollutant Load (L)

In the case of barley, L was higher in the second period regardless of the approach applied (A1-a or A1-b), due to an increase in the AR. For A1-b, considering the weather, soil and crop management factors, estimated L values were 30% higher than for A1-a (α = 10) (Table 2).

L was equal to zero in the soybean production using A1 because the crop was not fertilised during the growing period (Table 2). The ecophysiological characteristics of the crop allowed the N requirements to be covered by the N available in the soil and BNF.

A2 estimated a negative L in barley and soybean (L = 0 was assumed), because the surplus was negative, as the offtake was higher than AR in all cropping periods (Table 2).

Table 2. Pollutant load (L) values obtained applying leaching/runoff fraction approaches (A1-a and A1-b) and surplus approach (A2) for barley and soybean crops in Tandil County, Buenos Aires province, Argentine Pampas Region, in 2019 and 2020.

		A1				A2	
		A1-a		A1-b			
						Surplus [4]	
		α [1]	AR [3] (kgN/ha)	α [1]	β [2]	AR [3] (kgN/ha)	Offtake [5] (kgN/ha)
Barley 2019		0.10	101.00	0.13	0.42	101.00	103.00
Barley 2020			115.00			115.00	153.00
Soybean 2020			0.00		0.43	0.00	248.00
L [6a]	(kgN/ha)	10.00		13.00		0.00	
L [6b]	(kgN/ha)	11.50		15.00		0.00	
L [6c]	(kgN/ha)	0.00		0.00		0.00	

[1] α is leaching/runoff fraction applied to fertiliser. In this case, 10 or 13% of N fertiliser was lost through leaching/runoff. [2] β is leaching/runoff fraction applied to surplus after plant uptake and harvest. In this case, 42 or 43% of total N surplus was lost through leaching/runoff. [3] AR is defined as nitrogen fertiliser application rate. [4] Surplus is N fertiliser available in soil after plant was harvested. [5] Offtake refers to amount of N fertiliser taken up from soil by harvested crop. [6] L is pollutant load (N fertiliser) entering a water body: [a] pollutant load by barley 2019, [b] pollutant load by barley 2020, [c] pollutant load by soybean 2020.

3.2. *Estimation of Pollutant Load through the Nitrogen Balance Approach*

Table 3 illustrates the main N inputs and outputs for barley and soybean crops. A3 determined the L-R, which we assumed as L, i.e., the amount of N with potential to mobilise to water bodies.

Table 3. Nitrogen balance in barley and soybean crops located in Tandil County, Buenos Aires province, Argentine Pampas Region, 2019 and 2020.

Nitrogen Balance	Barley 2019	Barley 2020	Soybean 2020
Inputs (kgN/ha)			
N_i [1]	80.00	85.00	86.00
AR [2]	101.00	115.00	0.00
BNF [3]	00.00	00.00	38.00
N_{min} [4]	16.00	18.00	124.00
Total	197.00	218.00	248.00
Outputs (kgN/ha)			
Offtake [5]	103.00	153.00	248.00
V [6]	1.50	1.50	0.00
L-R (L) [7]	39.00	27.00	0.00
Total	143.50	181.50	248.00

[1] Initial nitrogen concentration available at sowing. [2] Nitrogen fertiliser application rate. [3] Soybean biological nitrogen fixation. [4] Nitrogen mineralization. [5] Amount of nitrogen taken up by harvested crop. [6] Volatilization of nitrogen fertilizer. [7] Nitrogen leaching/runoff assumed as L.

3.2.1. Estimation of Pollutant Load through the Nitrogen Balance Approach: Inputs

Regarding the inputs, AR was the main source of N-input to barley, accounting for 51–53% of total input. The N_i available at sowing was also determined as an important N input flow for crops (Table 3). In the case of barley, N_i accounted for 40 and 39% of the total input for 2019 and 2020, respectively, while in soybean it accounted for 35% of the total. The BNF in soybean was low, considering that in Argiudoll soils of the southeast APR only about 30% of the accumulated N is derived from BNF [55]. The high N_{min} levels of soil and N_i suggest that BNF was inhibited, because the plant used the available N in soil to cover its N requirement. Table 3 shows that N_{min} was the main source of N in the case of the soybean crop, which amounted to 50% of the inputs, and in barley it was the third most important source. The variations in N_{min} values between crop periods were related to soil moisture and T variability.

The Nan values indicate an optimal concentration of potentially mineralisable N in barley and soybean plots [43,56]. However, in the period between barley emergence and the end of the critical stage, Pp was very low and the average T was close to 9.5 °C (Figure 2). This reduced the supply of N_{min} to barley and increased the N supply from other sources. In soybean, high temperature during the summer and increased soil water content due to higher precipitation had a significant influence on the increased N_{min} rate (Figure 2) [43,56,57].

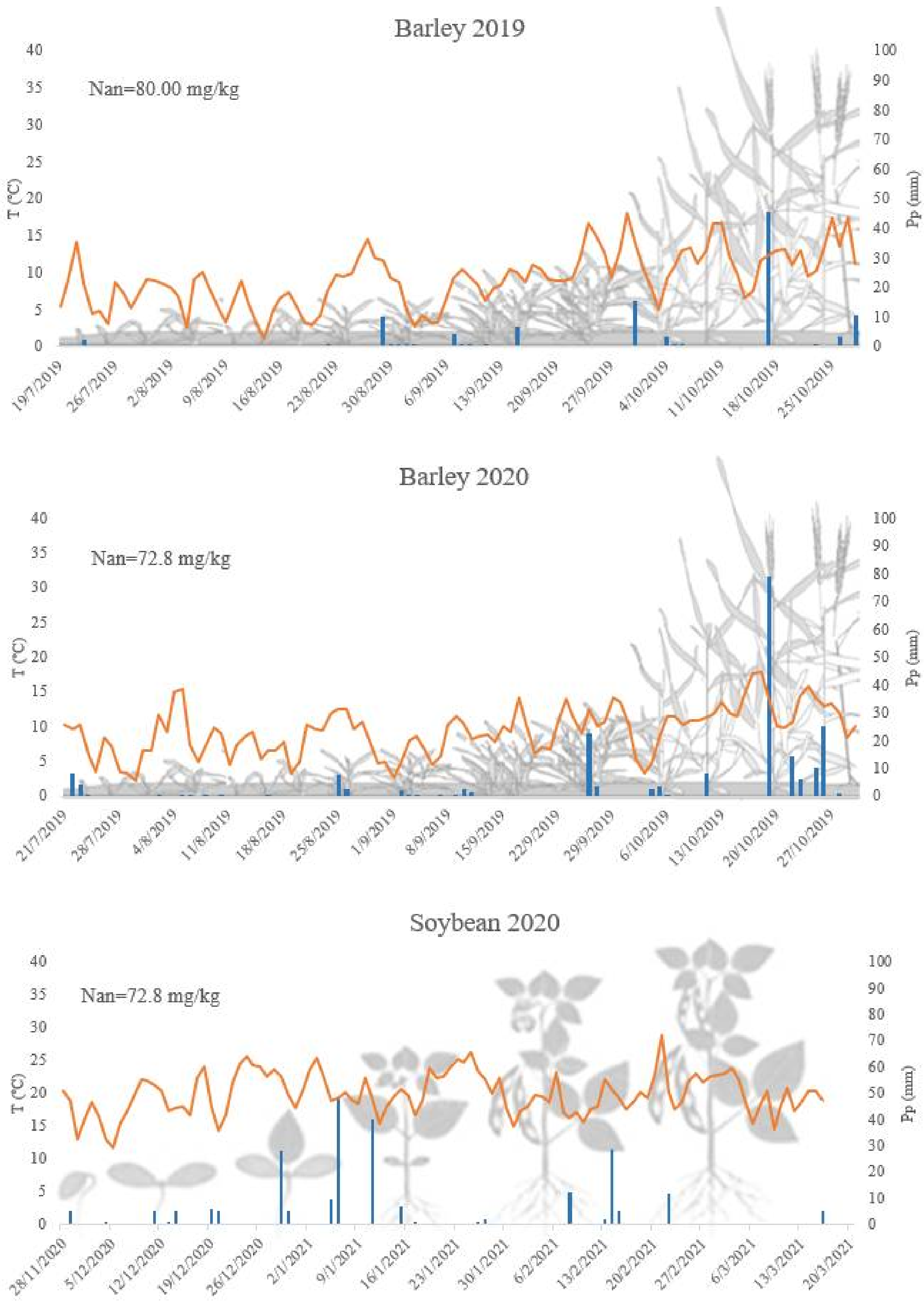

Figure 2. Anaerobic nitrogen (Nan) values and evolution of daily air temperature (T) (orange line) and daily precipitation (Pp) (blue column) during period of major nitrogen mineralisation and offtake by the crop. Illustration source: [58,59].

3.2.2. Estimation of Pollutant Load through the Nitrogen Balance Approach: Outputs

The offtake produced the major N output from the agroecosystem (Table 3). The barley crop in 2019 had Nc of 19 kgN/t and Y equal to 5.3 t/ha, and in 2020 registered Nc of 18 kgN/t and Y of 8.6 t/ha. This indicates an improvement in N use efficiency that can be attributed to a higher volume of Pp and a better distribution of Pp events during the campaign. The increase in Y in the 2020 period determined a greater N offtake.

The soybean plot had a higher Nc than the barley plot: Nc of 73 kgN/t, and Y of 3.4 t/ha. This value in line with studies carried out on soybean in the APR, which vary in a range from 60 to 80 kgN/t [45,46,60].

The losses due to ammonia nitrogen (N-NH_3) V of fertiliser were taken from representative literature on the APR, where this variable was estimated for winter crops under similar weather and edaphic conditions. Particularly, in the southeast of the APR soils, the V from winter crops is less than 1.5 kg N/ha for inputs of 120 kg N/ha due to the strong soil buffering power [47,48]. In addition, rainfall of more than 10 mm allows fertilisers to be incorporated into the soil profile [61].

The L-R proportion depended mainly on the amount of N offtake by the crop. In the first barley period, the difference between total N inputs and offtake for barley was greater, thus the N availability in the soil with leaching/runoff potential was increased. In the second barley period, the N offtake practically equalled the total N inputs, resulting in a lower N proportion available in the soil after the harvest.

In the case of soybean, the L-R was considered zero, because the N extracted by the plant was provided by the soil (N_i + N_{min}). The rest of the N requirement was incorporated by BNF.

The balances were positive in both barley periods, allowing accumulation of N in the soil for eventual availability in the next crop season.

3.3. Grey Water Footprint Applying the Three Approaches for Assessing Pollutant Load: Performance in Barley and Soybean Crops

Different GWF results were obtained applying different L estimation approaches. For the 2019 barley campaign, the N balance approach (A3) estimated the largest GWF value, which was 285 and 196% higher compared to the leaching/runoff fraction of A1-a and A1-b, respectively (Figure 3). Doubling the L values doubled the GWF results. The importance of correctly defining the L estimation approach should be noted.

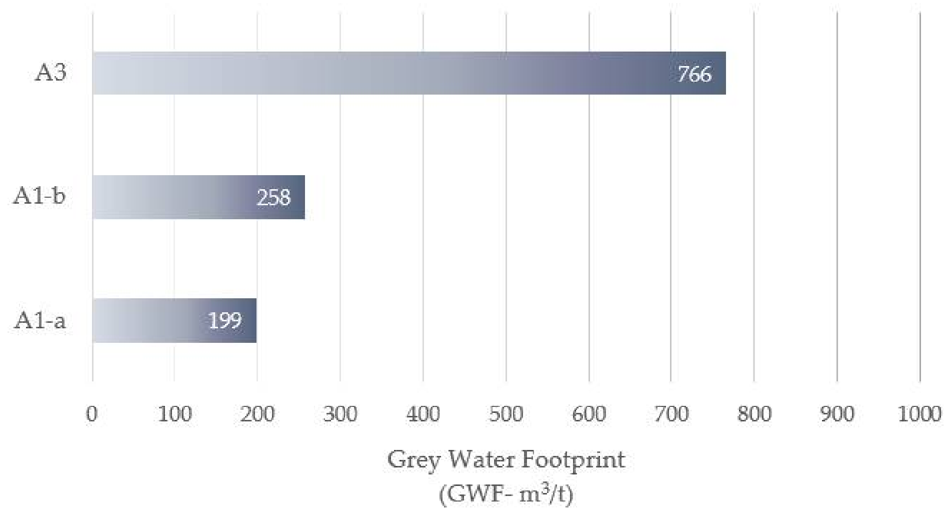

Figure 3. Grey water footprint (GWF) volume in barley crop during 2019 growing period using different calculation approaches. Leaching/runoff fraction approach (A1): A1-a: α = 10%, A1-b: α as a function of weather, soil and crop management factors; and N balance approach (A3). Surplus approach (A2) could not be applied for GWF estimation, because it estimated a negative contaminant load (L = 0).

The GWF volume for barley in 2020 was lower than in 2019, regardless of the approach used (Figure 4). This points to an increase in N use efficiency during 2020, since AR was similar to the 2019 campaign, but Y was 3300 kg/ha larger. The same as the previous period, A3 obtained a water footprint value 135 and 81% higher than A1-a and A1-b, respectively.

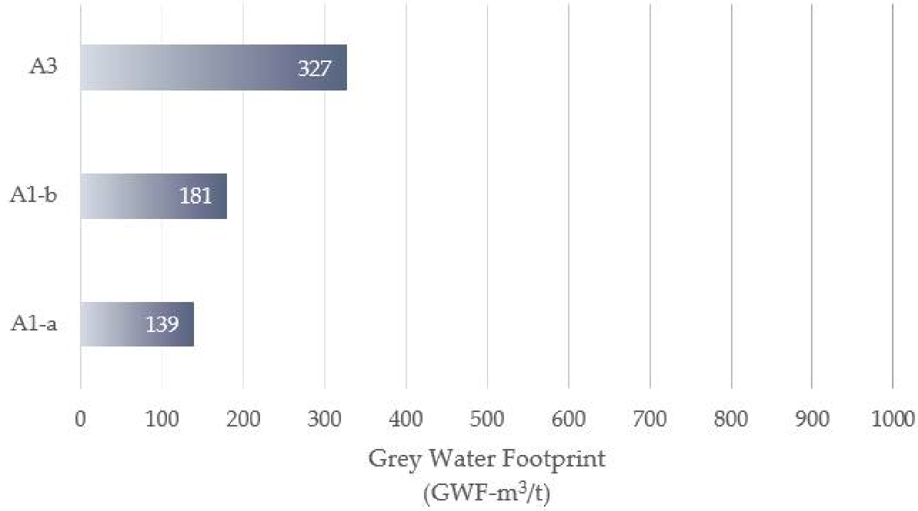

Figure 4. Grey water footprint (GWF) volume in barley crop during 2020 growing period using different calculation approaches. Leaching/runoff fraction approach (A1): A1-a: α = 10%, A1-b: α as a function of weather, soil and crop management factors; and N balance approach (A3). Surplus approach (A2) could not be applied for GWF estimation, because it estimated a negative contaminant load (L = 0).

Finally, the GWF of barley according to A2 could not be estimated. In this case, the approach conceptually did not represent the crop management practices, where N offtake exceeded AR. Thus, there was no N surplus from the soil, and L was zero or negative (Table 2).

In the case of soybean, the GWF associated to nitrogen was zero applying A1, A2 and A3, because there was no N fertiliser application. The plant used the N from the soil and completed the total N requirement through BNF. Thus, there was no N surplus in the soil.

4. Discussion

4.1. Evaluation of the Three Approaches for Assessing Pollutant Load: Performance in Barley and Soybean Crops

The three L (and therefore GWF) estimation methods have strengths and weaknesses (Table 4). In the case of the leaching/runoff fraction approach (A1-a), due to the non-availability of data, a constant value of α = 10 for different regions and crops is generally considered. That is, 10% of the applied fertiliser is lost through leaching/runoff. However, in practice, this fraction is not constant. It depends on environmental factors, crop type and agricultural practices, making it intrinsically variable, both spatially and temporally [9,16,62]. In addition, Laspidou [20] indicated that the GWF is sensitive to the value of α and that doubling α doubles GWF. Consequently, assuming the same value of α for an entire region can produce imprecise GWF values [16,22].

Approaches 1 and 2 consider fertilisation as the only N input to the system and source of leaching/runoff. This simplified assumption of potential losses of chemical products can lead to inaccurate results [16].

In our study, A1 and A2 did not, in general, represent the N dynamics, nor fertiliser behaviour observed in barley and soybean.

Particularly for barley, it is necessary to adjust AR because an excess of N can alter the proportion of protein in grain [63]. In Argentina, commercial production of malting barley crops must comply with quality standards, including a grain protein percentage in a range between 9.5 and 13% [64]. Any grain that does not satisfy this requirement receives significant price discounts, causing a problem for the farmer.

Table 4. Strengths and weaknesses of three grey water footprint assessment methods analysed: leaching/runoff fraction, surplus and the balance approach.

Pollution Load Estimation Method	Strengths	Weaknesses
Leaching/runoff fraction approach	Applicable to pesticides, herbicides and fungicides [1] Requires less input data Applicable at regional and global scales	Generally considers a constant value of α = 10 (A1-a) Considers fertilization as the only N input and output Estimates at a lower level of detail
Surplus approach	Applicable to pesticides, herbicides and fungicides [1] Applicable at regional and global scales	Considers fertilization as the only N input and output Requires more input data Functional only in cases where crop can offtake compound
N balance approach	Considers different N input and output flows in plant–soil–atmosphere system	Requires more input data Preferably applicable at local and medium scales

[1] Applicable to pesticides, herbicides and fungicides, as these compounds do not exist naturally in the environment and anthropogenic application is the only input to the system.

Soybean produced in the southeast of the APR was previously inoculated to favour N fixation. Fertiliser use can induce the crop to substitute N derived from BNF with N fertiliser, increasing production costs [46,65–67]. National and international studies suggest that fertiliser application may be justified in high yielding environments. However, in Argentina, the United States and Brazil, the relationship between soybean price and N fertiliser price does not favour fertiliser application in this crop [46,68–70].

To define the AR in barley, soybean and other crops in the APR, the N concentration of the soil at sowing is considered. Therefore, the N in the soil (N_i-N_{min}) and BNF (legumes) cover the crop requirements, and the rest is compensated by AR [71–76]. This explains two issues:

A. The AR in soybean and barley is adjusted according to the crop requirements and the environmental capacity. This management increases the efficiency of fertilisation, e.g., in the case of the barley, AR was high, but Y was high in 2019 and very high in 2020, while nitrogen fertilization was not necessary for soybean. This fertilisation practice reduces the fertiliser availability in the soil and consequently the fertiliser proportion that leaches or runs off to surface and groundwater bodies. However, this does not mean that there is not N leaching/runoff generated by other N inputs, such as mineralisation. Therefore, A1-a and A1-b may not be appropriate for estimating L in barley and soybean crops. In addition, A1-b calculated α using a much higher Ppm value (800 mm) than the Pp during the crop period (100.80 and 203.30 mm in barley 2019 and 2020 and 198.90 mm in soybean in 2020). Pp is a highly influential factor in the leaching/runoff process. Applying a Ppm value contributes to the overestimation of fertiliser loss through leaching/runoff.
B. In both crops, the AR will always be lower than the N offtake by the plant, because the N available in the soil also contributes to crop growth. This calls into question the L estimation by A2. In this study, A2 was complemented by A3 to determine the L-R as a residual term of the N balance.

Unlike the two previous approaches, the N-balance approach (A3) incorporates the concept of nutrient cycling, thus considers the different N input and output flows in the plant–soil–atmosphere system. Therefore, A3 indicates the existence of other N input sources besides fertiliser, such as the N_i available at sowing and N_{min}, which affect the N availability in the soil. Both N fluxes were equally important in proportion to fertilisation, and even conditioned the AR applied by the farmer. Consequently, the application of A3 allowed us to capture the N dynamics and weight of each process in the partitioning of this element within the agroecosystem, including the actual N proportion with potential to leach or run off to water bodies. Therefore, A3 would provide the most accurate estimate of L compared to A1 and A2.

Finally, the application of A1 and A2 for L estimation can be perfectly applicable in the case of pesticides, herbicides and fungicides. Unlike N, these compounds do not exist naturally in the environment and anthropogenic application is the only input to the system.

4.2. N Balance Approach: The Importance of Initial N Concentration and Mineralization in Pollution Load Estimation

A3 indicated the existence of N sources equally important to fertilisation, such as N_i available at sowing and N_{min}, which affect the N availability in the soil. Both inputs conditioned AR, as described in the previous section. By contrast, previous studies following A1 and A2 did not consider these N sources for determining L and GWF, while Mekonnen and Hoekstra [7], applying A3, only considered fertilisers and manure as the main N inputs to the production system.

In our study case, N_i represented between 35 and 40% of the N input to crops [55]. N_{min} was high in soybean during the summer, when it provided about 50% of the N required by the plant and inhibited the BNF.

The N_{min} from soil organic matter provides an important amount of N available for crop production [57,77]. Some authors agree that it provides between 50 and 80% of the crop's N demand, especially in humid and temperate environments with high organic matter content in the soil, such as the southeast of the APR [56,78,79].

N_{min} values have been recorded in different soils around the world. Martinez [57] determined mean N_{min} values in a range from 56.1 to 168.7 kg/ha in Typic Argiudoll of the APR for wheat and barley cultivation under direct seeding. Egelkraut et al. [77] estimated a net N_{min} of 26 to 67 kg/ha in Typic Kandiudult in the United States under conventional tillage. Dharmakeerthi et al. [80] found a net N_{min} of 103 to 145 kg/ha on Typic Hapludalf soil in Canada. Karyotis et al. [81], in an analysis of 13 soil types of Greece, determined N_{min} of 36.6 to 212.8 kg/ha.

As indicated in A3, L-R derives from three N input sources: AR, N_i and N_{min}. Therefore, including only AR would probably underestimate L.

We can consider that N_i and N_{min} are natural N sources that provide N to the system with or without human intervention. However, agricultural practices affect both variables and these can result in higher N mobilisation and increased GWF volume. Recent studies in the APR reported that a proportion of N leaching/runoff is a product of N_{min} [82–85]. This debate requires an in-depth and interdisciplinary analysis, which is outside the scope of this study.

N_i and N_{min} are spatially and temporally heterogeneous; therefore, they are obtained by point soil analysis of the study area. These variables are not easy to obtain and reduce to an average for global GWF estimates; nevertheless, they are necessary variables to generate accurate and representative estimates. For this reason, we believe that local studies can contribute to optimising the L calculation and favour subsequent data extrapolation.

4.3. Study Scales in Pollutant Load Assessment and Grey Water Footprint

L and GWF assessments at global, provincial, country and regional scales have been on the forefront and provided reference values [12,13,18,21]. However, when the scale of analysis is increased, there is a tendency to homogenise the variable values involved in the estimation and apply simpler estimation models such as A1 or A2, which require less input data but reduce the quality and precision of the results [16].

In particular, in the GWF estimation, the AR and Y data used are often average data with values generalised by region. This can lead to inexact interpretations of GWF volume and its potential impact [16,22]. In this sense, recent studies have proposed using remote sensing as a tool to improve the spatial estimation of the water footprint; such is the case of Y [24,31].

A3 requires more input data and preferably a local or medium scale of analysis due to the heterogeneity of the variables. However, it allows a considerably detailed scale of analysis, which is necessary to understand the dynamics of processes involved in L. This is essential to extrapolate estimates at the regional or landscape scale, especially for an emerging study topic such as GWF, where uncertainties are still important.

Finally, GWF estimates will depend on the approach and the quality of the input data. The spatial and temporal variability of parameters such as leaching/runoff fraction, AR, Y and Cnat suggest that studies be carried out at a more localised scale.

4.4. Grey Water Footprint Values Compared with the Literature

The GWF values for barley obtained in the present study were compared with the global average value of 131 m^3/t obtained by Mekonnen and Hoekstra [13,21]. In the 2019 period, the values for barley (A1-a = 199 m^3/t, A1-b = 258 m^3/t, A3 = 767 m^3/t) were above the world average, whereas in the 2020 period, the values (A1-a = 139 m^3/t, A1-b = 181 m^3/t, A3 = 327 m^3/t) were closer to the world average. Mekonnen and Hoekstra [13,21] estimated the GWF of crops applying A1-a (α = 10) to calculate L and assuming Cnat equal to zero. As observed in the Results section and as mentioned by other authors, a leaching/runoff fraction of 10% tends to underestimate the GWF value [7,22]. Mekonnen and Hoekstra [7] reinforced this point when they estimated higher GWF volume applying α of 18% and Cnat of 0.0004 kgN/m^3. Despite its relevance, some studies did not employ the leaching/runoff fraction, which implies that the total application rate is mobilized into water bodies, overestimating the GWF values [23,86,87].

The soybean crop did not generate a GWF associated with nitrogen fertiliser consumption, because its fertilisation is not a frequent practice in the southeast of the APR. Similarly, in the rest of the country, the amount of N provided by fertilisers is insignificant in relation to the total nutrient demand [23,55]. This is in line with the results obtained by Ercin [88], who reported a GWF of zero in inoculated soybean grown in Canada. Reis et al. [89] determined an average GWF volume of 38.9 m^3/t for soybean cultivation in the São Carlos municipality, Brazil. Finally, Mekonnen and Hoekstra [13,21] suggested a global average GWF value equal to 37 m^3/t for soybean, lower than most crops. These studies suggest that, globally, the GWF associated with N use in soybean is low. However, this does not imply that soybean crops do not affect water resources. In Argentina, the use of endosulfan and glyphosate in soybean production has contributed significantly to groundwater contamination [36,38,90–92]. Consequently, we believe it is necessary to include these compounds in future soybean GWF calculations.

5. Conclusions

This study analysed three methodologies proposed in the literature to assess the nitrogen-related pollutant load (L) and grey water footprint (GWF) using local data on barley and soybean plots in the Argentinean Pampas: (1) leaching/runoff fraction approach, (2) surplus approach and (3) nitrogen balance approach. According to the results obtained, the N balance approach is the most representative and reliable method to estimate nitrogen-based L and GWF, as it incorporates the nutrient cycling concept and N partitioning in the agroecosystem. The other two approaches might not be appropriate, as they consider fertiliser application as the only N source. Nevertheless, when the GWF is estimated for other substances, such as pesticides, herbicides and fungicides that do not exist naturally in the environment, those approaches can also be accurate and suitable. These conclusions can be extrapolated to GWF assessment not only in Argentina but also in other parts of the world.

Homogenising the L calculation method contributes to optimising GWF estimation, generating comparable results and favouring complementary studies for regional GWF estimations. This is essential for decision-makers to be able to count on robust information to promote in public policies that contribute to constant monitoring and preservation of water resources. On the other hand, it is also important to promote studies at the local scale. Understanding these processes at the micro scale is the first step in obtaining the appropriate estimation at the regional or landscape scale, especially in a recent field such as the GWF, where there are still many unknowns.

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