



Accounting for the Assimilative Capacity of Water Systems in Scotland

Paula Novo ^{1,2}

Article

- ¹ Land Economy, Environment and Society Group, Scotland's Rural College (SRUC), Edinburgh EH9 3JG, Scotland, UK; paula.novo@sruc.ac.uk; Tel.: +44-(0)-1315354037
- ² Social, Economic and Geographical Sciences Group, The James Hutton Institute, Aberdeen AB15 8QH, Scotland, UK

Received: 16 June 2017; Accepted: 21 July 2017; Published: 26 July 2017

Abstract: A key methodological challenge in understanding the relationship between the economy and the underlying ecosystem base resides in how to account for the ecosystem's degradation and the decline of associated ecosystem services. In this study, we use information on nutrients and metals concentrations from the Environmental Change Network (ECN) database and the Scottish Environment Protection Agency (SEPA) for the period 2000–2010 in order to assess the assimilation capacity of water systems. The research covers five upstream sites and 17 downstream sites in northeast Scotland. Our results highlight the relevance of considering a number of pollutants, and suggest that elements such as arsenic, lead and mercury can pose a threat to ecosystems' sustainability and health. However, little research has been done in terms of their assimilation capacity and their impact on grey water footprint assessments. In addition, the results indicate that background conditions might be relevant when performing sustainability analysis at different spatial scales. The study also poses relevant questions in relation to land management approaches versus traditional 'end-of-pipe' water treatment approaches, and the definition of maximum and background concentrations. In this regard, further studies will be required to understand the trade-offs between different ecosystem services depending on how these concentrations are defined.

Keywords: water quality; water pollution level; assimilative capacity; grey water footprint; nutrients; metals; Scotland

1. Introduction

The benefits of water quality and its impact on ecosystems have led water to become a policy priority in many parts of the world [1–3]. Water pollution is intrinsically linked to ecosystems' health, the delivery of ecosystem services and human well-being [4]. As such, there is an increasing interest in accounting for both the contribution of water resources to the economy and the impact the economy has on water systems [5,6]. In this respect, a number of papers have applied the environmental Kuznets curve (EKC) to examine the relationship between income and pollution [7–9]. However, empirical evidence of an inverted U-shape relationship between economic growth and pollution has been mixed [6–9]. In particular, in the case of water resources, Miglietta et al. [6] have shown that there is no evidence of an inverted U-relationship between economic growth and water use, when using the Water Footprint (WF) as a water use indicator.

Considerable experience exists with water quantity accounts in national accounting systems, as reflected in the System for Environmental Economic Accounts Central Framework (SEEA, CF), which is the standardised system for environmental accounting [10]. However, less experience exists regarding the inclusion of water quality issues in standardised environmental–economic accounts. Although a number of initiatives exist to progress in the development of water quality accounts [5], methodological challenges still remain, such as the definition and measurement of water quality

classes [10]. So far, water quality accounts are still experimental in the SEEA-Water [1] and describe only the total change in quality for the accounting period.

The quality of water may be approached in terms of its uses and functions or in relation to certain quality standards, as in the case of the EU Water Framework Directive [5]. The water footprint concept has been increasingly used to account for the impact that consumption and production patterns have on water resources [11]. The WF measures the volume of freshwater embedded in consumption and/or production, as well as water quality issues [11–13]. While green and blue water footprints are defined in terms of consumptive water, the grey water footprint (GWF) is defined as the volume needed to assimilate a pollutant load on a water body based on natural background concentrations and existing water quality standards [11]. The GWF is thus an indicator of pollution from anthropic activity [14]. In this respect, the water footprint, including green, blue and grey, provides a wider indicator of the impacts of human activity on the quantity and quality of water resources. Thereby, it allows combining both policy targets and ecological information.

The GWF approach has been useful to capture trends in social and economic pressures on water resources [14–16], and to provide an indication of the assimilative capacity of water ecosystems and their role as sinks. However, previous publications [17,18] have shown that assumptions on the natural concentration of pollutants in water bodies largely influence the GWF results, and that heterogeneity aspects are often overlooked [19]. Thus, most studies often set a value for natural concentration that is fixed across space and time. In this paper, we take into account spatial and temporal variations in the concentration of pollutants, and use upland sites as benchmarks to account for the effect of geochemical conditions on the assimilative capacity of the receiving water body.

In this article, we examine the evolution of water quality and the assimilative capacity of water bodies in northeast Scotland, which is a necessary step for the assessment of the GWF. For this purpose, we use information on water quality from the Environmental Change Network (ECN) [20] database and the Scottish Environment Protection Agency (SEPA) [21] for the period 2000–2010. The ECN database provides information on freshwater quality in upland areas, while SEPA reports water quality downstream at the outlet of the catchment. As the geological features of a particular site strongly influence the content of chemical elements released into freshwater bodies, water quality indicators in upland areas where there is little anthropogenic influence can provide useful information on background and environmental conditions.

Our results offer new insights to the WF literature by highlighting the relevance of considering a number of pollutants and the role of background concentrations. So far, most studies on grey water footprint have focused on key nutrients such nitrogen and phosphorus. However, the results presented in this study suggested that pollutants such as arsenic, lead and mercury can pose a threat to ecosystems' sustainability and health, while little research has been done in terms of their water footprint. The paper is organized as follows. Section 2 describes the methods and materials used. Section 3 presents the main results, and Section 4 discusses the findings.

2. Materials and Methods

2.1. Materials

In this paper, we make use of two databases: the Environmental Change Network (ECN) [20] database and the Harmonised Monitoring Scheme (HMS) from the Scottish Environment Protection Agency (SEPA) [21]. The ECN comprises 45 freshwater and 12 terrestrial sites distributed across the UK. This research focusses on five freshwater sites in northeast Scotland: Lochnagar, Loch Kinord, Loch Leven, Birnie Burn (Glensaugh) and Spey at Fochabers. The studied database covers the period 2000–2010. ECN freshwater chemistry information consists of a collection of samples from standing and running waters (or automatic recording where appropriate) that measures physical variables of aquatic environmental importance.

Data from SEPA have been obtained through the CUAHSI HydroDesktop administered at The James Hutton Institute. The database includes freshwater chemistry for 55 sites spread across Scotland. In this paper, we use information from 17 sites located in northeast Scotland for the period 2000–2010 (see Figure 1).

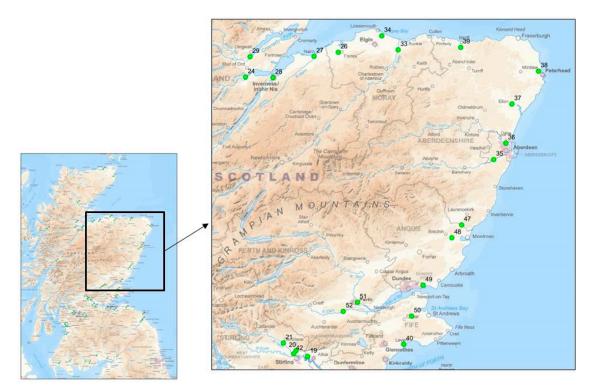


Figure 1. Location of Scottish Environment Protection Agency (SEPA) downstream sites. The data points included in this study are: (26) Findhorn; (27) Nairn; (28) River Ness; (33) River Spey; (34) River Lossie; (35) River Dee; (36) River Don; (37) River Ythan, (38) River Ugie; (39) River Deveron; (40) River Leven; (47) Rier North Esk; (48) River South Esk; (50) River Eden; (51) River Tay and (52) River Earn. Note: numbering of sites corresponds to the Harmonised monitoring scheme site number.

The study includes monthly values for the following geochemical variables: (i) nutrients: ammonium, nitrate, phosphorus, and phosphates; and (ii) metals: aluminium, arsenic, chloride, copper, iron, manganese, mercury, nickel, lead, sodium, sulphate, and zinc. Maximum allowed concentrations in water bodies have been taken from the Directive 98/83/EC, amended by Regulation (EC) N° 596/2009 of the European Parliament, and the guidelines for the quality of drinking water by the World Health Organization [22] and Scottish Public Drinking Water Regulations [23]. In this respect, maximum concentration has been established in relation to drinking water standards. It should be noted that for some water quality variables, ecological standards can be more restrictive than drinking water standards. However, in general for comparative studies, it is recommended to use the same standard throughout the study. Thus, while natural and pollutant concentrations in water bodies vary across time and space, maximum concentrations are set according to the regulations.

2.2. Methods

The GWF is an indicator of water resources appropriation through pollution. In this respect, it is defined as the volume required to dilute any chemical substances above established ambient quality standards [11,13,14]. Similar to the GWF approach, in this paper we estimate the capacity that water bodies have to assimilate pollution. This assimilative capacity is presented as a ratio between the pollutant concentration in the water body (*C*, in mass/volume) and the difference between the water

quality standard (the maximum acceptable concentration C_{max} , in mass/volume) and the background concentration (C_{back} , in mass/volume), as expressed in Equation (1).

$$MAC = C/(C_{max} - C_{back}), \tag{1}$$

where MAC = Maximum Assimilative Capacity, C = pollutant concentration in the water body, C_{max} = acceptable concentration (mg/L), and C_{back} = background concentration (mg/L).

If MAC is equal to 1, the system is operating at the limit in which the capacity to deal with pollution is the same as the pollution level. If the ratio is higher than 1, the pollution level is higher than the capacity, thus yielding to a system under stress. When the ratio is lower than 1, the pollution is below the assimilation capacity.

In this study, we estimate MAC at the outlet of the catchment. Estimates of the ration between pollutant concentration and maximum acceptable concentration for upland sites enable us to assess the assimilative capacity in 'pristine' upland areas. As shown in Cruz and Andrade [24], the estimation of natural background concentrations is key for deriving threshold levels. Water quality measures at the outlet of the catchment allow us to take into account both point and diffuse pollution along the catchment. The load at this point will include contamination from different sources; consequently, this method does not allow us to allocate concentrations to different sources. In addition, in case of decay processes, concentrations will be lower downstream, which in turn would imply that the sink capacity of the catchment in some parts will be underestimated.

Regarding background concentrations C_{back} , references 13 and 25 recommend using local data for natural background concentrations [13,25]. In this study, pollutant concentrations in upland areas, which are considered in a status close to 'pristine', are used as background concentrations to estimate the MAC at the outlet of the catchment.

3. Results

3.1. Water Quality in Upland Systems

Data from the ECN database enable us to analyse the evolution of water quality in the selected upland systems for the period 2000–2010. We focus on a number of nutrients and metals for which EU and Scottish drinking water regulations, and World Health Organization guidelines, establish maximum concentrations. Thus, comparison between the actual concentrations and the maximum allowed substance concentrations provide an indication of the capacity of the system to function as a sink. Table 1 reports the maximum values used in this study.

Element	C _{max} (mg/L)
Nutrients	
NH_4^+	0.5
NO_3^{-}	50
Ptot	0.1
PO_{4}^{3-}	0.1
Metals	
Cl	250
SO_4^{2-}	250
Mn	0.05
Fe	0.2
Ni	0.02
Hg	0.001
Cu	2
Zn	3
Pb	0.01
As	0.01

Table 1. Maximum concentrations	(C_{max})) used in ratio	calculations.
---------------------------------	-------------	-----------------	---------------

Note: Over 0.1 mg/L there might be problems of eutrophication in streams and rivers. For lakes values are lower and assimilation capacity might be underestimated in those cases. Source: Based on EU Council Directive 98/83/EC and Scottish Public Drinking Water Regulations.

Figure 2 shows the ratio between the concentration of nutrients (ammonium, nitrates, phosphorus and phosphate) and the maximum allowed concentrations. Values represent median daily estimates in instances where more than one measurement was performed in a day. As it can be observed, in the case of ammonium the ratio is below 0.5, which means that the capacity of the system is always over 50%. That is, the system is able to cope with current concentrations of ammonium. This same result is observed for nitrates. The results for all four ECN sites analysed in this study indicate that nitrate concentration represents less than 5% of maximum allowed concentrations in water bodies. In the case of phosphorus and phosphates, it is worth noting that the system is often under more stress, with ratios surpassing 0.5 in many cases, and 1 in the case of Loch Leven, Spey and, to a lesser extent, Birnie Burn. These sites are also located lower in the catchment and are therefore most likely to be exposed to diffuse pollution from domestic and agricultural sources.

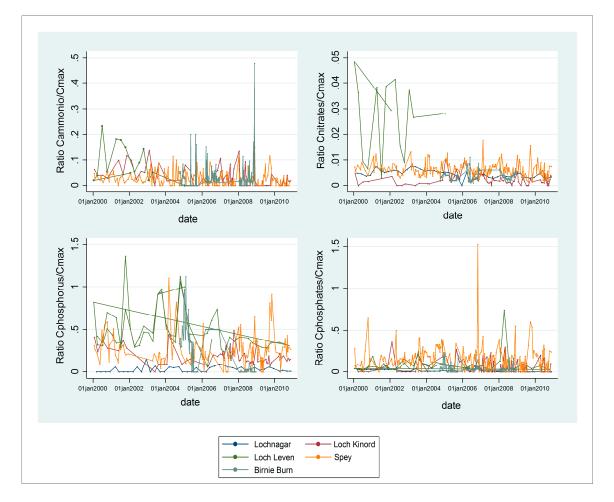
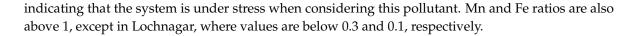


Figure 2. Median monthly ratio between concentration of nutrients and maximum concentrations in Environmental Change Network (ECN) sites. Source: Own elaboration based on ECN data and drinking water quality standards (Directive 98/83/EC, Scottish Public Drinking Water Regulations [23]).

Figure 3 shows the median ratio between the actual concentration of metals and the maximum concentration established by the drinking water standards. We report those metals for which maximum concentrations have been established in regulations. Data for sodium (Na), nickel (Ni) and arsenic (As) are also available, but have not been reported in Figure 3 as these data are not available for most sites during the period covered by this analysis (2000–2010). The results indicate that, except in the cases of aluminium (Al), manganese (Mn) and iron (Fe), metal concentrations are below the maximum allowable concentrations. In the case of Al, ratios are above 1, except for Lochnagar, where average ratio is 0.14. Al ratios for Spey are the highest, with an average value of 1.2 and a maximum of 16.3,



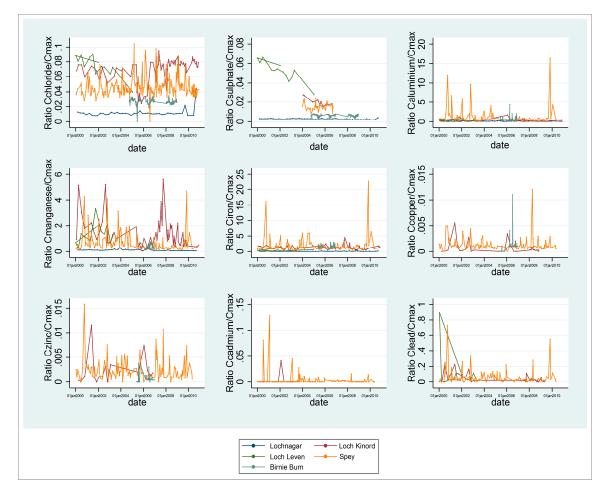


Figure 3. Median monthly ratio between concentration of metals and maximum concentrations in ECN sites. Source: Own elaboration based on ECN data and drinking water quality standards (Directive 98/83/EC, Scottish Public Drinking Water Regulations [23]).

Interestingly, it is worth noting that at Lochnagar, most elements are out of the potable water ranges due mainly to low (aprox. 5.5–6) pH values. This may be consistent with previous studies e.g., Yang et al. [26,27] that showed that Lochnagar and its catchment were contaminated by anthropogenic-derived trace metals since the 1860s. The source of these contaminants is mostly from atmospheric deposition from anthropogenic sources. According to Yang et al., ochnagar presented high concentrations of mercury (Hg), lead (Pb), zinc (Zn), copper (Cu) and cadmium (Cd), with soils rich in organic matter and able to accumulate large amounts of trace metals [26]. Thus, soil erosion and subsequent mobilisation results in high concentrations of metals in Lochnagar.

Data for Na is only available for Spey and Loch Kinord during the period 2000–2010, and for Birnie Burn between 2005 and 2007. Although ratio estimates are not plotted in Figure 3, the values are in all cases below 0.08. Ni data are only available for Spey (for the whole period), for Loch Kinord (2000–2003) and Loch Leven (2003). Despite limited data, in most cases the ratio estimates are below 0.2, with a maximum value of 0.31 in Loch Kinord in 2001. Arsenic estimates are only available for Spey and Loch Kinord, with values below 0.1 except in the years 2000 and 2001, when the ratios oscillated between 0.1 and 0.2.

3.2. Water Quality Downstream: Nature or Nurture?

Table 2 reports average (with standard deviation) and maximum values of the ratio between the actual concentration of nutrients and the maximum allowed concentration at the outlet of a number of catchments in northeast Scotland for the period 2000–2010. The actual values have been measured in downstream points, as shown in Figure 1. As it can be observed, phosphorous and phosphates are critical substances in all the catchments, with ratios above 1 in many cases, indicating that these water bodies are under stress with regards to phosphorous concentration. In this respect, phosphorous run-off from agricultural lands is one of the main sources of diffuse pollution [28,29] and can accelerate eutrophication of water bodies. In addition to phosphorous, ammonium (NH_4^+) shows average values above 0.5 and with a maximum of 1.5 in the River Don. The maximum value for ammonium is also above 1 in the River Leven and above 0.5 in the Rivers Ugie, Deveron and North Esk.

Site	\mathbf{NH}_4^+	NO_3^-	Ptot	PO_4^{3-}
Findhorn	0.016 (0.015)	0.004 (0.003)	0.219 (0.530)	0.112 (0.198)
	0.089	0.019	5.140	1.960
Nairn	0.028 (0.051)	0.033 (0.015)	0.458 (2.348)	0.128 (0.127)
	0.526	0.061	24.200	0.720
Ness	0.014 (0.015)	0.004 (0.002)	0.104 (0.274)	0.065 (0.082)
	0.100	0.016	3.61	0.870
Spey	0.023 (0.021)	0.006 (0.003)	0.247 (0.167)	0.173 (0.118)
	0.116	0.018	1.1	0.65
Lossie	0.113 (0.070)	0.048 (0.011)	0.385 (0.190)	0.273 (0.327)
	0.378	0.069	1.29	3.43
Dee	0.041 (0.038)	0.016 (0.009)	0.239 (0.175)	0.131 (0.122)
	0.168	0.043	1.02	1.04
Don	0.534 (0.297)	0.063 (0.013)	0.791 (0.405)	0.623 (0.318)
	1.526	0.091	2.37	1.62
Ythan	0.070 (0.066)	0.150 (0.017)	0.593 (0.376)	0.455 (0.251)
	0.364	0.189	3.01	1.82
Ugie	0.111 (0.098)	0.108 (0.018)	0.928 (0.523)	0.639 (0.305)
	0.546	0.165	3.33	1.87
Deveron	0.056 (0.065)	0.061 (0.016)	0.526 (0.326)	0.409 (0.219)
	0.642	0.099	2.73	1.41
Leven	0.085 (0.122)	0.034 (0.018)	0.770 (0.432)	0.184 (0.153)
	1.278	0.094	2.86	1.03
North Esk	0.082 (0.093)	0.039 (0.014)	0.502 (0.546)	0.197 (0.187)
	0.68	0.086	3.3	1.4
South Esk	0.083 (0.051)	0.036 (0.013)	0.649 (0.621)	0.272 (0.247)
	0.336	0.066	5	1.4
Dighty Water	0.084 (0.055) 0.264	0.146 (0.026) 0.215	n.a.	0.454 (0.366) 2.7
Eden	0.140 (0.091)	0.127 (0.017)	2.314 (1.617)	1.576 (0.938)
	0.52	0.173	15.4	5.3
Тау	0.038 (0.033)	0.012 (0.009)	0.228 (0.150)	0.074 (0.101)
	0.24	1.126	1.11	0.8
Earn	0.062 (0.051)	0.025 (0.010)	0.435 (0.223)	0.207 (0.179)
	0.4	0.051	1.33	1.1

Table 2. Average ratio (std. dev.) and maximum value of the ratio between actual nutrient concentrations and maximum allowed concentrations in downstream sites. Period 2000–2010.

Source: Own elaboration based on data from SEPA and drinking water quality standards (Directive 98/83/EC, Scottish Public Drinking Water Regulations [23]).

Table 3 presents the average ratios comparing the actual concentrations for several metals with respect to the maximum allowable concentrations in drinking water. These ratios have been estimated at the outlet of the catchment. We only include metals for which data are available in more than one site. Thus, estimates for Cu and Zn are not presented in this table, as data are only available for Spey,

with average estimates of 0.825 and 0.386, respectively. In addition, values for Na are close to zero, and have not been included in Table 3, either. As it can be observed, ratios are above 1 for As in all the studied sites, indicating that actual concentration at least doubles allowable concentration, and the system is not able to cope with this pollution up to drinking water standards. It should be noted that As concentrations are only available for the period 2000–2010 in Leven and between 2005–2010 in the rest of the sites, except in north and south Esk, Eden, Tay and Earn, where data are available between 2002 and 2010. In the case of Pb, values are also above 0.5 in the Dee and Spey, and above 1 in the rest of the sites during the period 2005–2010. Similarly, Hg ratios are also above 0.5 in all the reported sites, and below 1 only in Findhorn and Ness. As in the case of As, Hg data are not available for the whole period 2000–2010, except in Lossie, Dee and Ugie.

Site	Cl	SO_4^{2-}	Mn	Fe	Ni	Hg	Pb	As
Findhorn	0.044 (0.014)	0.010 (0.004)				0.768 (0.319)		6.922 (4.227)
Nairn	0.075 (0.020)	0.024 (0.010)				1.040 (0.624)		13.024 (5.338)
Ness	0.048 (0.197)	0.008 (0.002)				0.666 (0.322)		5.213 (2.813)
Spey	0.047 (0.013)	0.016 (0.006)	0.020 (0.013)	0.279 (0.212)	0.035 (0)	2.507 (1.933)	0.632 (0.347)	8.358 (1.959)
Lossie	0.127 (0.038)	0.060 (0.013)	0.029 (0.018)	0.370 (0.316)	0.073 (0.079)	2.055 (0.938)	3.058 (2.683)	25.79 (6.138)
Dee	0.050 (0.018)	0.024 (0.008)	0.025 (0.017)	0.267 (0.154)	0.030 (0.020)	1.514 (1.860)	0.665 (0.382)	8.813 (2.254)
Don	0.105 (0.024)	0.052 (0.015)	0.128 (0.179)	0.202 (0.168)	0.325 (0.121)	3.097 (3.123)	1.147 (1.910)	22.428 (4.444)
Ythan	0.136 (0.030)	0.072 (0.014)	0.026 (0.012)	0.139 (0.114)	0.410 (0.120)	2.900 (2.113)	1.113 (0.726)	28.329 (3.249)
Ugie	0.164 (0.023)	0.072 (0.018)	0.029 (0.017)	0.323 (0.298)	0.163 (0.088)	2.786 (1.695)	2.432 (1.414)	28.341 (2.968)
Deveron	0.103 (0.028)	0.044 (0.014)	0.015 (0.004)		0.194 (0.057)	1.528 (0.926)		21.118 (3.119)
Leven	0.104 (0.046)	0.422 (0.256)						46.486 (17.391)
N Esk	0.044 (0.013)	0.031 (0.009)				1.435 (0.969)		11.657 (2.476)
S Esk	0.041 (0.013)	0.030 (0.007)						11.867 (2.631)
Dighty Water	0.136 (0.029)	0.095 (0.009)						
Eden	0.118 (0.020)	0.128 (0.022)						39.387 (5.565)
Тау	0.029 (0.008)	0.015 (0.006)	0.008 (0.006)		0.037 (0.007)	0.786 (0.329)		7.184 (1.456)
Earn	0.033 (0.012)	0.020 (0.008)				1.334 (0.680)		10.211 (2.706)

Table 3. Average ratio (std. dev.) between metals' concentrations and maximum allowed concentrations in downstream sites. Period 2000–2010.

Source: Own elaboration based on data from SEPA and drinking water quality standards (Directive 98/83/EC, Scottish Public Drinking Water Regulations [23]).

Next, we present the results obtained for the ratio between the actual concentration of nutrients and metals in downstream sites, and the maximum allowed concentration as set in drinking water standards [23]. Compared to the results presented in Tables 2 and 3, these estimates take into account background concentrations, assuming these concentrations are equal to the concentrations of nutrients and metals in upstream (ECN) sites. It should be noted that, where available, we also made use of

background concentrations for metals as reported in Peters et al. [30]. Table 4 shows the upstream sites used as reference in each downstream site and the average concentrations in each upstream site both from the ECN database [20] and from Peters et al. [30]. Median monthly values were used to estimate monthly ratios between actual nutrient concentrations, maximum allowed concentrations as set in drinking water standards [23] and background concentrations in downstream sites as per Table 4. The results presented in Figure 4 indicate that ammonium ratios are in most cases below 0.4, with only a few values above that threshold. Similarly, nitrates' ratios are the lowest, with values below 0.1 during the whole period 2000–2010. As shown earlier in Table 2, phosphorus ratios are above the assimilative capacity of the water body, based on maximum concentrations as defined by drinking water standards. The highest values for phosphates are observed in the Don, while total phosphorus values peak in the River Leven downstream in the catchment.

Table 4. Upstream sites used as reference for background concentrations in downstream sites. Background concentrations (μ g/L).

ECN Sites	SEPA Sites	NH_4^+	NO_3^-	P _{tot}	PO ₄ ³⁻	C1	SO_4^{2-}	Mn	Fe	Ni	Hg	Cu	Zn	Pb	As
Spey	Findhorn Nairn Ness Lossie	11	317	25	16	116	3811	35	377	1	0.01	2	7 2	0.5	0.3
Lochnagar	Dee Don	-	221	3	1	2882	687	5	9	0.13 0.3	-	2 0.3	2	-	0.09 0.2
Leven	Leven	44	131	49	8	18,647	13,182	71	78	1	-	0.7	1.2	1	-
Birnie Burn	North Esk South Esk	9	169	25	4	6681	1589	20	76	0.3	-	1 0.6	2 0.1	-	-

Source: Own elaboration based on ECN data for the period 2000–2010 and Peters et al. [30]. Note: These values have been obtained from Peters et al. [30] for Findhorn, Dee, Don, Leven, North & South Esk.

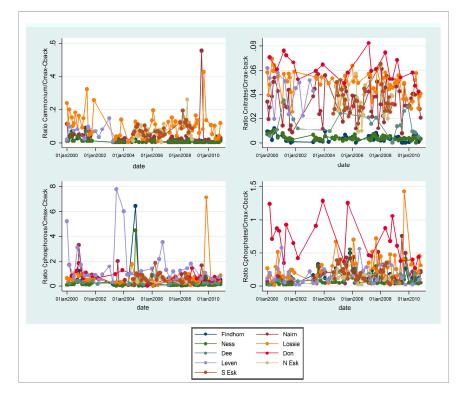


Figure 4. Median monthly ratio (std. dev.) between actual nutrient concentrations, the maximum allowed concentrations and background concentrations in downstream sites. Source: Own elaboration based on SEPA and ECN data and drinking water regulations (Directive 98/83/EC, Scottish Public Drinking Water Regulations [23]).

Figure 5 provides a closer look at the ratio between actual phosphorus concentrations and the maximum concentrations when background concentrations are or not taken into account. This allows us to compare the effect of background concentrations on the assimilative capacity of the system for this particular case. As it can be observed, ratios are slightly higher when background concentrations are taken into account, indicating that background or upstream values can play an important role in reducing the capacity of water bodies to assimilate pollution and supply ecosystem services.

Table 5 shows the average ratios (standard deviation) between the concentration of a number of metals and the maximum allowed concentrations in drinking water. The ratio also takes into consideration background concentrations in water bodies, assuming that these concentrations are equal to the values in reference upstream sites (as per Table 4). In addition, values from Peters et al. [30] have been taken into account when available. It should be noted that calculations have been done on a monthly basis. Thus, in some cases, either downstream or upstream values were not available and it was not possible to obtain ratio estimates. For example, lead concentrations for the Dee and Don are available between 2005 and 2010, while upstream values are only available until 2005. In these cases, assumptions would need to be made with respect to any of the missing values. However, this is out of the scope of this study. As it can be observed from the table, the iron (Fe) ratio in Lossie is negative because the levels of background concentrations used exceed maximum allowed concentrations based on drinking water standards. In line with the results presented in Table 3, As ratios are the highest, suggesting that the system is unable to cope with As concentrations up to a drinking water standard.

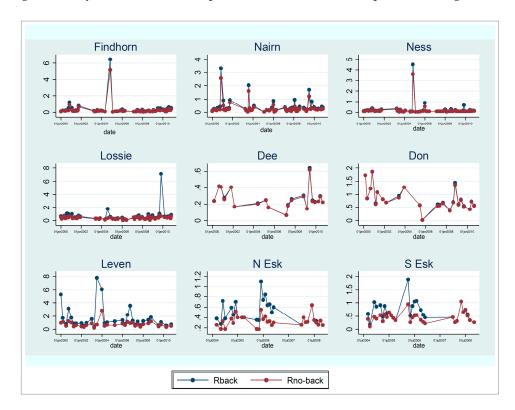


Figure 5. Median monthly ratio (std. dev.) between actual phosphorus concentrations and maximum allowed concentrations, with (Rback) and without (Rno-back) background concentrations in downstream sites. Source: Own elaboration based on SEPA data, ECN data, and drinking water regulations (Directive 98/83/EC, Scottish Public Drinking Water Regulations [23]).

Site	C1	SO_4^{2-}	Mn	Fe	Ni	Hg	Pb	As
Findhorn	0.046 (0.014)	0.012 (0.003)	-	-	-	0.715 (0.260)	-	7.414 (4.668)
Nairn	0.080 (0.020)	0.028 (0.008)	-	-	-	1.059 (0.643)	-	14.107 (5.587)
Ness	0.050 (0.144)	0.009 (0.001)	-	-	-	0.600 (0.238)	-	5.526 (3.142)
Lossie	0.135 (0.039)	0.062 (0.013)	0.002 (0.226)	-2.18 (9.96)	0.087 (0.097)	2.044 (0.929)	3.304 (2.911)	27.548 (6.622)
Dee	0.049 (0.016)	0.023 (0.007)	0.023 (0.021)	0.241 (0.139)	0.030 * (0.01)	-	-	8.991 * (2.013)
Don	0.108 (0.023)	0.055 (0.013)	-	0.185 (0.064)	0.331 * (0.124)	-	-	23.001 * (4.643)
Leven	0.145 (0.128)	0.498 (0.353)	-	-	-	-	-	-
North Esk	0.043 (0.010)	0.030 (0.008)	-	-	-	-	-	-
South Esk	0.042 (0.010)	0.031 (0.005)	-	-	-	-	-	-

Table 5. Average ratio (std. dev.) between actual metal concentrations and maximum allowedconcentrations in downstream sites, including background concentrations. Period 2000–2010.

Source: Own elaboration based on data from SEPA, drinking water quality standards (Directive 98/83/EC, Scottish Public Drinking Water Regulations [23]), ECN data and * Peters et al. [30] for background concentrations.

4. Discussion

This study assesses the capacity of a number of water bodies to assimilate pollution. Although the study uses data from Scotland, there are a number of key findings that might be relevant for other regions and scales of analysis. Our results highlight the relevance of considering a number of pollutants when estimating the assimilative capacity of water systems and, subsequently, the GWF. So far, most studies on grey water footprint have focussed on key nutrients (mainly nitrogen and phosphorus). However, the results presented in this study suggested that other pollutants such as arsenic, lead and mercury can pose a threat to ecosystems' sustainability and health, while little research has been done in terms of water footprint. This is in line with Franke et al. [13], in which the authors assess the GWF of key pollutants, including mercury, vanadium and ammonium. In addition, the research also assesses the assimilative capacity in areas with no apparent anthropogenic influence. The results show that the relationship between actual pollutant concentrations and the maximum allowed concentrations defined by the set standard, in this case drinking water quality regulations, in the region is important to understanding the pollution potential of areas without industrial activities nearby. In addition, it shows an application of the assimilative capacity as an indicator of environmental change.

The GWF and assimilative capacity of water systems present a relatively simple estimate to analysing water quality data, assessing the sustainability of water systems, and defining hotspots to target policy actions. The results presented above reinforce the importance of covering different spatial and temporal scales due to variations between catchments and periods of time. Thus, for example, the study shows that phosphorous is a main issue not only in downstream sites but also in upland areas. In this respect, reference sites that are located lower in the catchment are most likely to be exposed to different sources of diffuse pollution. Therefore, more targeted management in the upland areas could provide cost-effective solutions to tackle downstream pollution [31]. In addition, the results show that background conditions are also relevant in some cases, with maximum assimilative capacity ratios displaying different values when these background conditions are taken into account. In this respect, the geochemistry of the site might be relevant when performing sustainability analysis. An aspect linked to this is the land cover in upstream sites. For example, research has shown that conifer afforestation in upland areas of Scotland is associated with increased levels of manganese in runoff [32]. Our results also point to high manganese concentration ratios in upland sites. In addition to these specific results, the study highlights the spatial differences that take place both across and within catchments. The results suggest that GWF studies would therefore benefit from more spatially explicit assessments in order to determine the most critical substance at different spatial scales.

In this study, we defined maximum concentrations according to drinking water standards. However, other thresholds could be defined based on a different set of criteria, such as the ecology of the water body, which could help understand better the trade-offs and priorities in terms of different ecosystem services. Along these lines, a relevant question would be whether a change in land management practices could be more cost-effective than an 'end-of-pipe' or traditional water treatment approaches. In this line, a natural step from this research would be to examine the cost of reducing pollution via land management compared to public preferences for improved water quality [33].

The MAC ratios presented in this study address both spatial and temporal heterogeneity. In this respect, several issues need further investigation. First, background concentrations have been assumed equal to upland concentrations, which might introduce some errors in the estimations. More evidence about the use of these concentrations to benchmark downstream concentrations needs to be undertaken. Second, trends over the 10-year period analysed in this study are difficult to define. Thus, it would be interesting to consider longer time series in order to identify temporal and spatial patterns. Third, some of the downstream water quality data display outliers that would need to be analysed in further detail to understand better their behaviour and economic and policy implications.

Finally, although a large volume of data are already available, this research shows that data are still lacking, in particular for longer and consistent periods of time, in a way that allows a better assessment of the dynamics and links between land management, geochemistry and water quality.

Acknowledgments: The work of Paula Novo has been funded by the Scottish Government Rural Affairs under the Environment Portfolio Strategic Research Programme 2011–2016, Theme 1 (WP1.3. Application of an ecosystem approach at a range of scales).

Conflicts of Interest: The author declares no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

References

- United Nations. SEEA-Water. System of Environmental-Economic Accounting for Water; Department of Economic and Social Affairs, Statistics Division, United Nations: New York, NY, USA, 2012; pp. 103–115.
- McGonigle, D.F.; Harris, R.C.; McCamphill, C.; Kirk, S.; Dils, R.; Macdonald, J.; Bailey, S. Towards a more strategic approach to research to support catchment-based policy approaches to mitigate agricultural water pollution: A UK case-study. *Environ. Sci. Policy* 2012, 24, 4–14. [CrossRef]
- Blackstock, K.L.; Martin-Ortega, J.; Spray, C.J. Implementation of the European Water Framework Directive: What does taking an ecosystem services-based approach add? In *Water Ecosystem Services: A Global Approach*; Martin-Ortega, J., Ferrier, R.C., Gordon, I.J., Khan, S., Eds.; Cambridge University Press: Cambridge, UK, 2015; pp. 57–64.
- Haines-Young, R.; Potschin, M. The links between biodiversity, ecosystem services and human well-being. In *Ecosystem Ecology: A New Synthesis*; Raffaelli, D., Frid, C., Eds.; BES Ecological Reviews Series; CUP: Cambridge, UK, 2010; pp. 110–139.
- Russi, D.; ten Brink, P. Natural Capital Accounting and Water Quality: Commitments, Benefits, Needs and Progress; A Briefing Note; The Economics of Ecosystems and Biodiversity (TEEB): Geneva, Switzerland, 2013.
- 6. Miglietta, P.P.; De Leo, F.; Toma, P. Environmental Kuznets curve and the water footprint: An empirical analysis. *Water Environ. J.* **2016**, *31*, 20–30. [CrossRef]
- 7. Cole, A.M. Trade, the pollution haven hypothesis and the environmental Kuznets curve: Examining the linkages. *Ecol. Econ.* **2004**, *48*, 71–81. [CrossRef]
- 8. Harbaugh, W.T.; Levinson, A.; Wilson, D.M. Reexamining the Empirical Evidence for an Environmental Kuznets Curve. *Rev. Econ. Stat.* **2002**, *84*, 541–551. [CrossRef]
- 9. Vehmas, J.; Luukkanen, J.; Kaivo-Oja, J. Linking Analyses and Environmental Kuznets Curves for Aggregated Material Flows in the EU. *J. Clean. Prod.* **2007**, *15*, 1662–1673. [CrossRef]
- 10. United Nations. *System of Environmental-Economic Accounting* 2012—*Central Framework;* United Nations: New York, NY, USA, 2014.
- 11. Hoekstra, A.Y.; Chapagain, A.K.; Aldaya, M.M.; Mekonnen, M.M. *The Water Footprint Assessment Manual: Setting the Global Standard*; Earthscan: London, UK, 2011.
- 12. Hoekstra, A.Y.; Chapagain, A.K. *Globalization of Water: Sharing the Planet's Freshwater Resources*; Blackwell Publishing: Oxford, UK, 2008.
- 13. Franke, N.A.; Boyacioglu, H.; Hoekstra, A.Y. *Grey Water Footprint Accounting: Tier 1 Supporting Guidelines;* UNESCO-IHE Institute for Water Education: Delft, The Netherlands, 2013.

- Miglietta, P.P.; Toma, P.; Fanizzi, F.P.; De Donno, A.; Coluccia, B.; Migoni, D.; Bagordo, F.; Serio, F. A Grey Water Footprint Assessment of Groundwater Chemical Pollution: Case Study in Salento (Southern Italy). *Sustainability* 2017, 9, 799. [CrossRef]
- 15. Hoekstra, A.Y.; Wiedmann, T.O. Humanity's unsustainable environmental footprint. *Science* **2014**, *344*, 1114–1117. [CrossRef] [PubMed]
- 16. Hoekstra, A.Y. The sustainability of a single activity, production process or product. *Ecol. Indic.* **2015**, *57*, 82–84. [CrossRef]
- 17. Liu, C.; Kroeze, C.; Hoekstra, A.Y.; Gerbens-Leenes, P.W. Past and future trends in grey water footprints of anthropogenic nitrogen and phosphorus inputs to major world rivers. *Ecol. Indic.* **2012**, *18*, 42–49. [CrossRef]
- 18. Wang, L.; Ding, X.; Wu, X. Letter to the Editor: Careful considerations when reporting and evaluating the grey water footprint of products. *Ecol. Indic.* **2014**, *41*, 131–132. [CrossRef]
- 19. Finger, R. Letter to the Editor: More than the mean—A note on heterogeneity aspects in the assessment of water footprints. *Ecol. Indic.* 2013, *29*, 145–147. [CrossRef]
- 20. ECN. UK Environmental Change Network. Available online: http://www.ecn.ac.uk/ (accessed on 18 May 2017).
- 21. Scottish Environment Protection Agency (SEPA). Harmonised Monitoring Scheme. Available online: http://www.hutton.ac.uk/research/themes/managing-catchments-and-coasts/consultancy/understanding-resources/harmonised-monitoring (accessed on 18 May 2017).
- 22. WHO. Guidelines for Drinking Water Quality, 4th ed.; World Health Organization: Genève, Switzerland, 2011.
- 23. The Scottish Government. *The Water Supplies (Water Quality) (Scotland) Regulations;* DWQR: Edinburgh, UK, 2014.
- Cruz, J.V.; Andrade, C. Natural background groundwater composition in the Azores archipelago (Portugal): A hydrogeochemical study and threshold value determination. *Sci. Total Environ.* 2015, 520, 127–135. [CrossRef] [PubMed]
- European Comission. Common implementation strategy for the Water Framework Directive (2000/60/EC). In *Guidance Document No. 27: Technical Guidance for Deriving Environmental Quality Standards*; Technical Report 2011-055; European Commission: Brussels, Belgium, 2011.
- 26. Yang, H.; Rose, N.L.; Battarbee, R.W. Distribution of some trace metals in Lochnagar, a Scottish mountain lake ecosystem and its catchment. *Sci. Total Environ.* **2002**, *285*, 197–208. [CrossRef]
- 27. Yang, H.; Linge, K.; Rose, N.L. The Pb pollution fingerprint at Lochnagar: The historical record and current status of Pb isotopes. *Environ. Pollut.* **2007**, *145*, 723–729. [CrossRef]
- White, P.J.; Hammond, J.P. Updating the Estimate of the Sources of Phosphorus in UK Waters. Defra Final Report for Project WT0701CSF. Available online: http://randd.defra.gov.uk/Default.aspx?Menu=Menu& Module=More&Location=None&ProjectID=13635 (accessed on 18 May 2017).
- Jackson-Blake, L.; Dunn, S.M.; Helliwell, R.C.; Skeffington, R.A.; Stutter, M.I.; Wade, A.J. How well can we model stream phosphorus concentrations in agricultural catchments? *Environ. Model. Softw.* 2015, 64, 31–46. [CrossRef]
- 30. Peters, A.; Merrington, G.; Crane, M. *Estimation of Background Reference Concentrations for Metals in UK Freshwaters;* Water Framework Directive—United Kingdom Technical Advisory Group (WFD-UKTAG): Edinburgh, UK, 2012.
- 31. Vinten, A.J.A.; Martin-Ortega, J.; Glenk, K.; Booth, P.; Balana, B.B.; MacLeod, M.; Lago, M.; Moran, D.; Jones, M. Application of the WFD cost proportionality principle to diffuse pollution mitigation: A case study for Scottish Lochs. *J. Environ. Manag.* **2012**, *97*, 28–37. [CrossRef] [PubMed]
- 32. Heal, K.V. Manganese and land-use in upland catchments in Scotland. *Sci. Total Environ.* **2001**, 265, 169–179. [CrossRef]
- 33. Glenk, K.; Lago, M.; Moran, D. Public preferences for water quality improvements: Implications for the implementation of the EC Water Framework Directive in Scotland. *Water Policy* **2011**, *13*, 645–662. [CrossRef]



© 2017 by the author. 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/).