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Authors(s)	O'Boyle, Shane, Quinn, Rebecca, Dunne, Noelle, Mockler, Eva M., Ní Longphuirt, Sorch
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Author(s): Shane O'Boyle, Rebecca Quinn, Noelle Dunne, Eva M. Mockler and Sorchá Ní Longphuirt

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Shane O'Boyle
(corresponding
author; email:
shane.OBOYLE@ec.
europa.eu), Environ-
mental Protection
Agency, McCumiskey
House, Richview,
Clonskeagh Road,
Dublin 14, Ireland;
(on secondment to
European Commis-
sion, DG Environ-
ment, Beaulieu,
Brussels, Belgium);
Rebecca Quinn, Envir-
onmental Protection
Agency, McCumiskey
House, Richview,
Clonskeagh Road,
Dublin 14, Ireland;
Noelle Dunne, Envir-
onmental Protection
Agency, McCumiskey
House, Richview,
Clonskeagh Road,
Dublin 14, Ireland;
Teagasc, Agriculture
and Food Develop-
ment Authority,
Johnstown Castle,
Wexford, Ireland; Eva
M. Mockler, UCD
Dooge Centre for
Water Resources
Research, University
College Dublin,
Dublin 4, Ireland;
Sorcha Ní Longphuirt,
Environmental
Protection Agency,
Inniscarra, Co. Cork,
Ireland.

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WHAT HAVE WE LEARNED FROM OVER TWO DECADES OF MONITORING RIVERINE NUTRIENT INPUTS TO IRELAND'S MARINE ENVIRONMENT?

**Shane O'Boyle, Rebecca Quinn, Noelle Dunne,
Eva M. Mockler and Sorcha Ní Longphuirt**

ABSTRACT

Excessive nutrient loading to the marine environment from different sources and pathways, including rivers, has led to nutrient over-enrichment and the phenomenon of eutrophication in estuaries and coastal waters. The systematic monitoring of riverine nutrient inputs to Ireland's marine environment began in 1990. Over this period there has been a large reduction in nutrient inputs with loads of total phosphorus, total ammonia and total nitrogen decreasing by 71.8% (4,716 tonnes), 77.3% (5,505 tonnes) and 39.0% (59,396 tonnes), respectively. The largest reductions, particularly in total phosphorus and total ammonia, were seen in the main rivers discharging to the Celtic and Irish Sea coasts, with smaller or no reductions in rivers discharging along the western and north-western Atlantic coast. The reductions indicate the success of measures to reduce nutrient loss but also the disproportionate reduction in phosphorus over nitrogen. The ratio between nitrogen and phosphorus loads has increased by 2.5% per year and by as much as 4.1% per year for discharges to the Celtic Sea. As a consequence, the stoichiometric N:P ratio of river inputs to the Celtic Sea has more than doubled. The potential for this disparity to create a nutrient imbalance in downstream estuarine and coastal waters is discussed.

INTRODUCTION

Eutrophication, the excessive growth of both phytoplankton and macroalgal blooms, caused by inputs of nutrients such as phosphorus (P) and nitrogen (N), is a widespread problem in the world's coastal seas. The proliferation of micro- and macroalgal blooms can displace other species and lead to the depletion of dissolved oxygen causing a general disturbance to the balance of organisms normally present (Kronvang *et al.* 1993; Boesch 2002; Dias and Rosenberg 2008). In Ireland, the problem of eutrophication in the marine environment is mostly restricted to estuarine areas with sixteen water bodies being classed as either eutrophic or potentially eutrophic in the most recent status assessment (Bradley *et al.* 2015). Nutrients that drive the process of eutrophication can come from a variety of sources including riverine and atmospheric inputs and direct discharges from municipal waste water treatment plants and industry (OSPAR 2010).

A number of policy instruments have been adopted to address the loss of nutrients from terrestrial sources. In a European context the most relevant legislation would be the European directives

on the provision of urban waste water treatment (UWWT Directive), the reduction of nitrates from agricultural sources and promotion of good agricultural practices (Nitrates Directive) and the licensing of industrial facilities (IPPC Directive). In 2000, the Water Framework Directive (WFD) was adopted; this provides a holistic framework for the management of water resources across freshwater, transitional and coastal systems.

In tandem with the development of legislative measures, a number of monitoring programmes were established to assess the nutrient status of surface waters and to quantify the loss of nutrients from terrestrial sources to the sea. In 1990, the Paris Convention established the Comprehensive Study of Riverine Inputs to better quantify on an annual basis river-borne and direct inputs of nutrients and other substances to the marine environment of the North-East Atlantic Ocean. In Ireland, a pilot programme was commenced in 1986 and 1987, focusing on riverine inputs to the Irish Sea (ERU 1989). In 1990, the pilot programme became a national programme and was extended to include rivers discharging to the Atlantic Ocean and Celtic Sea.

The estimation of nutrient loads to estuarine and coastal waters is an essential component of any

strategy to address the issue of nutrient enrichment and the management and restoration of impacted waters. In this paper we will report on the main findings of the national riverine inputs monitoring programme that is now over two decades old. This will involve a statistical trend analysis of the time series together with a discussion on the implications of these findings for the broader management of Ireland's aquatic environment.

MATERIAL AND METHODS

THE STUDY AREA

The national riverine inputs monitoring programme is managed by the Irish Environmental Protection Agency (EPA). The design of the programme followed the Comprehensive Study on Riverine Inputs and Direct Discharges (RID) principles (OSPAR 1998). Nineteen river catchments, representing some of the largest river catchments nationally, were selected (Fig. 1). A number of smaller river catchments were also included for different reasons. For example, the rivers Dodder and Tolka, which have relatively small catchments, were included because of the interest in the discharge of waste to the Liffey Estuary and Dublin Bay. The Avoca River was included in the programme because of the high metal concentrations which the 1989 Pilot Study had shown it to carry. In the case of the river Shannon, sampling was carried out on both the power station tailrace (Shannon TR) and on the old river channel (Shannon OC) as there is no accessible sampling point between the location where these sections rejoin and the tidal limit. Some smaller catchments were also included for logistical reasons as they were located between large river catchments and therefore were convenient to sample (i.e. Fergus, Maigue and Deel).

The proportion of the total catchment area to the sampling point in nearly all cases is greater than 80% with the notable exception of the catchment areas of the Slaney, Suir and Blackwater rivers, where the proportions covered are less than 75% (Table 1). In the calculation of loads, it has been assumed that the concentrations of the various nutrients recorded at the sampling stations are representative of those at the freshwater limits. As such, the nineteen rivers in the programme are considered to represent nutrient loadings from 63% (44,820 km²) of Ireland's total catchment area.

SAMPLING AND ANALYSIS METHODOLOGIES

Over the course of our study, sampling was usually undertaken in the first and last three months of each

year. This approach was intended to increase the frequency of sampling during periods of higher flows. The bulk of the annual loads are expected to be carried in such flows. A single sampling event was undertaken in the middle of the year when low flows were more likely to occur. Low flow concentrations are of greatest interest from the point of view of water quality since dilution of wastes is lowest at such times. In 2007, the sampling frequency was increased to monthly to align with the national Water Framework Directive monitoring programme. Samples were returned directly to the laboratory on the day of sampling or the following morning by courier and analysed within 24 hours of collection.

Samples were analysed for total phosphorus (TP); molybdate reactive phosphorus (MRP), also referred to as total reactive phosphorus (TRP); total oxidised nitrogen (TON); total ammonia (TA); Kjeldahl nitrogen and suspended solids. Oxidised nitrogen (nitrite plus nitrate) and Kjeldahl nitrogen (total ammonia plus organic nitrogen) were added to give total nitrogen (TN). The phosphorus and nitrogen parameters were measured using a Technicon Autoanalyser II system preceded, in the case of total phosphorus and Kjeldahl nitrogen, by a digestion step (the acid-persulphate method for the former and the acid sulphate/red mercuric oxide method for the latter). Phosphates were measured on unfiltered samples, the determination being therefore, total MRP. Nitrogen containing substances were also measured on unfiltered samples. Suspended solids were measured gravimetrically following filtration. All parameters were measured according to Standard Methods for the Examination of Water and Wastewater (2005) and earlier.

RIVER FLOWS

The hydrometric stations that provided the required data on river flows are shown in Fig. 1. Stage data were recorded from staff gauges at these points or in some cases extrapolated from automatic stage recorders within the catchment. These stage readings were subsequently converted to flow values based on stage discharge relationships established for these hydrometric monitoring points. In the case of the rivers Erne, Liffey and Shannon, flows were derived totally or partially from the hydro-electric stations. The proportion of the total catchments represented at the gauging stations are generally above 80%, the most notable exceptions being the Slaney and the Suir river catchments, where the proportions covered are less than 75%. Total catchment flows were calculated using the ratios of total catchment to gauged catchment areas.

Fig. 1—River catchments and hydrometric stations involved in the OSPAR Comprehensive Study on Riverine Inputs and Direct Discharges (RID). Area of catchment monitored indicated in dark grey, unmonitored area downstream of monitored area indicated in light grey and unmonitored catchments indicated in green.

Table 1—Location and percentage (%) of catchment monitored by each of the riverine monitoring stations in the national river inputs monitoring programme.

No.	River	Catchment (km ²)	Monitored (km ²)	(%)	Station Location	Station Code
1	Avoca	652	639	98	Upstream of Bridge on M11	10A03-1050
2	Bandon	608	492	81	Inishannon Bridge	20B02-0900
3	Barrow	3067	2760	90	Tinnahinch Bridge	14B01-3500
4	Blackwater	3324	2427	73	Lismore Bridge	18B02-2600
5	Boyne	2695	2560	95	Boyne at Oldbridge (Obelisk Br)	07B04-2200
6	Corrib	3138	3107	99	Quincentennial Bridge	30C02-0460
7	Deel	486	486	100	Deel at Askeaton Br	24D02-1450
8	Dodder	113	108	96	Footbridge, Beaver Row	09D01-0900
9	Erne	4372	4372	100	Erne at Cathleen's Falls	36E01-1600
10	Fergus	1042	782	75	Doora Bridge	27F01-0700
11	Lee	1253	1140	91	Leemount Bridge	19L03-0700
12	Liffey	1256	1118	89	Chapelizod Bridge	09L01-2350
13	Maigue	1052	810	77	Castleroberts Br	24M01-0900
14	Moy	2086	1919	92	Ardnaree Bridge	34M02-1100
15	Nore	2530	2378	94	Brownsbarn Bridge	15N01-2400
16a	Shannon OC	11700	11115	95	Athlunkard Bridge	25S01-2600
16b	Shannon TR	-	-	-	Tailrace, Parteen Weir	25S01-2900
17	Slaney	1762	1269	72	Enniscorthy Lower Bridge	12S02-2350
18	Suir	3610	2635	73	Kilsheelan Bridge	16S02-2700
19	Tolka	146	128	88	Footbridge, Griffith Park	09T01-1150

CALCULATION OF LOADS

The loads of the different substances have been calculated as the product of the flow-weighted annual mean concentration and the annual flow, in accordance with the RID principles (OSPAR 1998). In the case where a substance is recorded below the limit of detection (LoD), the RID principles indicate that two load estimates should be given in such cases, one based on assuming a zero concentration (lower estimate) for the samples in question and the other using the detection limit as the appropriate concentration (upper estimate).

SEA AREAS AND EXTRAPOLATION

For reporting purposes, loads from individual rivers are combined and reported on a sea area basis. The three areas used are the Irish Sea from the border with Northern Ireland to Hook Head; the Celtic Sea from Hook Head to Loop Head and the Atlantic from Loop Head to the border with Northern Ireland.

Loads in unmonitored areas are estimated by extrapolation from those calculated for relevant main rivers on the basis of catchment areas. Unmonitored areas were matched with catchments with similar characteristics. The size of the monitored and unmonitored areas draining to the three

sea areas represent 63% (44,820km²) and 37% (25,531km²), respectively, of the total area draining to the OSPAR maritime area (70,351km²).

STATISTICAL TREND ANALYSIS

A Mann-Kendall test was used to assess trends in annual flow-normalised loads of TP, MRP, TN, TON and TA between 1990 and 2013 from monitored areas. Annual flows were simply normalised using the ratio between these flows and the annual Long-Term Average flow (Table 2). Analysis of trends in the ratio between different nutrient loads was also undertaken. Loads in tonnes were converted to a molar equivalent to allow for a more meaningful stoichiometric interpretation of the change in the ratio between loads of the main nutrients.

Comparisons were also made of average annual loadings during the most recent three-year period (2011–13) and the first three-year period (1990–92) of the programme and as a measure of 'change from peak' to the maximum three-year average loading value over the time-series. A three-year average was used to reduce 'noise' in the annual values. Running three-year averages were calculated and calculations were based on monitored and unmonitored areas.

Table 2—Long-term average (LTA), minimum and maximum flow for each of the riverine monitoring stations. Period over which LTA is based is also shown and the sea area into which each river discharges is also indicated.

<i>River</i>	<i>LTA – 2011</i> [$\text{m}^3 \text{s}^{-1}$]	<i>Minimum Flow Rate</i> [$\text{m}^3 \text{s}^{-1}$]	<i>Maximum Flow Rate</i> [$\text{m}^3 \text{s}^{-1}$]	<i>LTA</i> (years)	<i>Sea Area</i>
Shannon (Tailrace)	156.0	0.5	414.9	79	Celtic Sea
Erne	102.7	1.1	321.9	60	Atlantic
Corrib	85.6	25.1	197.8	57	Atlantic
Blackwater	83.2	10.3	370.4	56	Celtic Sea
Suir	80.1	29.5	295.6	56	Celtic Sea
Moy	61.9	15.4	205.3	35	Atlantic
Shannon (Old Channel)	47.7	16.1	376.8	27	Celtic Sea
Barrow	45.5	10.5	185.4	15	Celtic Sea
Lee	42.8	1.3	221.7	55	Celtic Sea
Nore	42.5	6.1	227.4	39	Celtic Sea
Boyne	39.5	2.6	302.2	71	Irish Sea
Slaney	32.8	7.6	137.3	56	Celtic Sea
Fergus	22.4	2.8	111.3	18	Celtic Sea
Bandon	21.2	3.1	203.3	34	Celtic Sea
Avoca	20.5	4.1	195.4	17	Irish Sea
Liffey	17.4	2.5	82.8	51	Irish Sea
Maigue	16.9	2.5	148.6	29	Celtic Sea
Deel	11.2	0.9	93.9	18	Celtic Sea

ESTIMATION OF DIRECT DISCHARGES

Direct discharges from point sources such as waste water treatment plants (WWTPs) and industrial discharges downstream of the riverine monitoring station and in unmonitored catchments were also estimated. Prior to this study an estimation of direct discharges of TN and TP had only been completed for the year 1990 and has been previously reported. Information from 2011–14 was used to provide a more up-to-date estimate of direct discharges of P and N for the purposes of this paper. Load information from WWTPs was based on the values in Annual Environmental Reports (AER) submitted to the EPA. If an AER was not available, load estimates were calculated from population equivalent (PE) values and nutrient production rates of $12\text{g person}^{-1}\text{day}^{-1}$ for N and $2\text{g person}^{-1}\text{day}^{-1}$ for P. Treatment efficiency factors followed international guidelines (OSPAR 2004). For industrial discharges, loads were estimated from an average of three years (2011–13) of TN and TP annual emission values reported to the Pollutant Release and Transfer Register. Facilities licenced by local authorities under Section 4 licences generally do not report annual emissions, and hence annual values were assumed as 25% of the license limits (OSPAR, 2004). Further details are available in Mockler *et al.* (2016, this issue).

LEVEL OF ACCURACY

The accuracy of riverine inputs measurements was assessed using a recent comparison of measured inputs of TN and TP against an estimation of nutrient lost. These data were derived from an independent source apportionment model applied to the Suir catchment in southern Ireland. The source load apportionment model (SLAM version 2.02, described in Mockler *et al.* 2016 (in this issue)) results were compared to measured loads at 16 stations in the catchment and were accurate to an average of 10% for TP and 4% for TN. The greater uncertainty in the modelled P estimates, compared to N, is likely due to the episodic nature of P losses and associated difficulties in monitoring loads (Jordan *et al.* 2007).

RESULTS

RIVERINE FLOW

Long-term average (LTA), minimum and maximum flow statistics are shown in Table 2. The river with the largest LTA flow was the Shannon ($203.7 \text{ m}^3 \text{s}^{-1}$) followed by the Erne ($102.7 \text{ m}^3 \text{s}^{-1}$), Corrib ($85.6 \text{ m}^3 \text{s}^{-1}$), Blackwater ($83.2 \text{ m}^3 \text{s}^{-1}$) and Suir ($80.1 \text{ m}^3 \text{s}^{-1}$). The smallest LTA flows were seen in the Deel ($11.2 \text{ m}^3 \text{s}^{-1}$), Maigue

Fig. 2—Annual and three-year running average annual national river loads (normalised) of (a,d) total phosphorus (TP), (b,e) total nitrogen (TN) and (c,f) total ammonia (TA) to the marine environment from monitored and unmonitored areas between 1990–2013.

($16.9 \text{ m}^3 \text{ s}^{-1}$), Liffey ($17.4 \text{ m}^3 \text{ s}^{-1}$) and Avoca ($20.5 \text{ m}^3 \text{ s}^{-1}$). The combined total LTA for the 19 rivers was $929.8 \text{ m}^3 \text{ s}^{-1}$, ranging between a minimum of $142 \text{ m}^3 \text{ s}^{-1}$ and maximum of $4092.0 \text{ m}^3 \text{ s}^{-1}$.

NATIONAL AND SEA AREA DISCHARGES

The annual and three-year average annual national loads of TP, TN and TA between 1990 and 2013 are shown in Fig. 2. National annual loads of all five nutrient parameters (TP, MRP, TN, TON and TA) showed a statistically significant decrease over the time series (Table 3). National loads of TP and TN decreased by 93 and 1,569 tonnes y^{-1} respectively over the time period (Table 3) equating to a decrease of 4.1% and 2.1% y^{-1} . Sea area discharges also showed a statistically significant decrease with the exception of loadings of TP and TON to the Atlantic, which were not significant. The only statistically significant increase was seen in MRP and TA loadings to the Atlantic, however, this increase may be due to an analytical issue which will be discussed in more detail below. In general,

the level of significance in trends was much higher for discharges to the Celtic and Irish Seas than to the Atlantic. This difference is also reflected in the rate of change in loads which are much higher for the Celtic and Irish Seas, than the Atlantic. The Irish Sea has seen the greatest percentage reduction per year across all five parameters but in absolute terms discharges to the Celtic Sea have seen the largest reductions with the exception of TA, which was higher for the Irish Sea (Table 3).

The ratios between different nutrient loads also showed some significant trends (Table 4). The molar load ratio between TN and TP (TN:TP) showed a significant upward trend, nationally and across each sea area. The increase in TN:TP reflects the greater relative reduction in loads of P in comparison to N. The greatest upward trend in the molar load ratio was seen in the discharges to the Celtic Sea, with the ratio between TN:TP increasing by as much as 4.1% per year. No significant trend was seen in the molar load ratio being discharged to the Atlantic. The molar ratio between TN and TA loads (TN:TA) showed a significant

Table 3—Trends in national and regional sea area river nutrient load between 1990 and 2013. Percentage (%) change per year is shown in parentheses. Analysis is based on flow-normalised annual data and monitored areas only. Grey text indicates a P-value > 0.05 which is considered not significant.

	National		Irish Sea		Celtic Sea		Atlantic	
	Tonnes Yr ⁻¹	P-value	Tonnes Yr ⁻¹	P-value	Tonnes Yr ⁻¹	P-value	Tonnes Yr ⁻¹	P-value
TP	-92.7 (-4.1)	<0.001	-18.3 (-5.3)	<0.001	-71.0 (-4.6)	<0.001	-2.7 (-0.8)	0.224
MRP	-48.8 (-4.1)	<0.001	-9.2 (-5.5)	<0.001	-37.7 (-4.5)	<0.001	1.9 (1.1)	0.050
TN	-1569.2 (-2.1)	<0.001	-600.5 (-3.6)	<0.001	-776.3 (-1.6)	0.002	-154.3 (-1.6)	0.035
TON	-737.3 (-1.4)	0.003	-180.4 (-1.6)	<0.001	-424.3 (-1.2)	0.016	-72.5 (-1.3)	0.056
TA	-185.7 (-7.5)	<0.001	-103.8 (-8.4)	<0.001	-37.9 (-3.6)	0.002	4.4 (2.4)	0.063

Table 4—Trends in national and sea area river nutrient load ratios between 1990 and 2013. Percentage (%) change per year (yr⁻¹) is shown in parentheses. Analysis is based on flow-normalised annual data and monitored areas only. Grey text indicates a P-value > 0.05 which is considered not significant.

	National		Irish Sea		Celtic Sea		Atlantic	
	Unit change Yr ⁻¹	P-value	Unit change Yr ⁻¹	P-value	Unit change Yr ⁻¹	P-value	Unit change Yr ⁻¹	P-value
TN:TP	2.5 (3.0)	0.002	3.1 (2.6)	0.021	3.4 (4.1)	<0.001	-0.1 (-0.2)	0.901
DIN:MRP	2.8 (2.5)	<0.001	5.7 (3.0)	0.001	3.8 (3.5)	<0.001	-1.8 (-2.3)	0.027
TP:MRP	0.0 (1.0)	0.050	0.0 (0.0)	0.941	0.0 (1.0)	0.206	-0.04 (-1.7)	0.003
TN:TON	0.0 (0.8)	0.014	-0.02 (-1.2)	<0.001	0.0 (0.7)	0.025	0.0 (0.0)	0.803
TN:TA	2.3 (5.1)	<0.001	4.1 (8.9)	<0.001	1.5 (2.5)	0.039	-1.7 (3.1)	0.007

Table 5—Statistical range of national (monitored and unmonitored) three-year average annual river load for each nutrient parameter between 1990 and 2013. The three-year period when maximum and minimum loadings occur is shown in parenthesis. The percentage (%) reduction from maximum and average load is also shown. Analysis based on flow-normalised data.

<i>Statistic</i>	<i>TP</i>	<i>MRP</i>	<i>TN</i>	<i>TON</i>	<i>TA</i>
Maximum	6,564 (1996–1998)	2,786 (1992–1994)	152,136 (1995–1997)	108,785 (1996–1998)	7,126 (1991–1993)
Minimum	1,848 (2011–2013)	1,237 (2011–2013)	92,740 (2011–2013)	72,161 (2011–2013)	1,622 (2004–2006)
Average	3,841	1,985	122,718	87,744	3,415
Percentage (%) reduction					
From maximum	71.8	55.6	39.0	33.7	77.3
From average	51.9	37.7	24.4	17.8	52.5

upward trend nationally and in loads discharging to the Celtic and Irish Seas. This reflects the greater reduction in TA loads relative to TN rather than an increase in TN. In the Irish Sea, the TN:TA molar load ratio increased by as much as $8.9\% \text{ y}^{-1}$ over the time period.

Comparing average annual nutrient loadings for the most recent three-year period (2011–13) to the maximum three-year period indicates how substantial the reduction in river nutrient loads has been to Ireland's marine environment. This is particularly evident for loads of TP and TA which have decreased by 71.8% (4,716 tonnes) and 77.3% (5,505 tonnes), respectively (Table 5). Loads of TN decreased by 39.0% from a peak of 152,136 tonnes representing a reduction of 59,395 tonnes. The figure for TA is skewed somewhat by inclusion of the figures for the Avoca River, which has seen a remarkable 99.2% reduction in TA following the introduction of a licensing regime in a large fertiliser production plant on the Avoca River in the late 1990s and the plant's closure in 2002. This reduction is responsible for the very substantial yearly percentage increase in the molar load ratio of TN:TA referred to above. If this reduction is removed from the national figures, the percentage reduction in national loads of TA from peak would be 59.2%.

TRENDS AND LOADS IN INDIVIDUAL RIVERS

Analysis of trends in nutrient loads in nineteen Irish rivers between 1990 and 2013 indicate a statistically significant downward trend in TP, TN and TA in the majority of rivers (Table 6). The largest and most significant downward trends in TP and TA were seen in the rivers discharging to the Irish and Celtic Seas with the exception of the River Lee and

River Bandon where no significant trend in TP was detected. No significant reductions in TP were observed in the rivers Corrib, Moy and Erne discharging to the Atlantic Ocean. The largest reductions in TN occurred in the rivers discharging to the Irish Sea and the River Lee, River Deel and River Maigue discharging to the Celtic Sea, with a smaller but still significant reduction in the Corrib and Erne. The only river to show an upward trend was the Corrib, which displayed an upward trend in TA. This statistically significant upward trend is likely to be an artefact related to a change in laboratory reporting. From April 2007, samples from the Corrib, Moy and Erne (from 2008) were sent to a different laboratory with a higher limit of detection for this parameter. The analytical LoD changed from 0.01 to 0.03 mg l^{-1} . As the majority of values from these rivers prior to April 2007 were already being reported at the existing LoD (i.e. 0.01 mg l^{-1}), any increase in the LoD may therefore be misinterpreted as a statistically significant increase in loading in these rivers. This also applies to MRP, as the LoD for this parameter also increased from 0.005 to 0.012 mg l^{-1} when sample analysis was moved to a different laboratory.

On an individual river basis it is evident from examination of Fig. 3 that loadings of TP and TA have shown the greatest reduction. For both TP and TA, the majority of rivers have seen a reduction $> 75\%$ and 70% , respectively. For the rivers Deel, Maigue, Suir, Nore, Dodder, Liffey and Tolka, the reduction in TP from peak has been $> 80\%$. Similar reductions in TA loads have been observed in the Maigue, Deel, Tolka, Suir and Avoca. For TN, the reduction observed in the majority of rivers was less than 50%, with only four rivers (Deel, Maigue, Tolka and Avoca) having a higher percentage reduction.

Table 6—Trends (Mann-Kendall) in river nutrient load to the marine environment between 1990 and 2013. The Shannon River is split into the Tail Race (TR) and Old Channel (OC) sections. Non-significant trends are indicated in grey.

River	Total Phosphorus			Total Nitrogen			Total Ammonia		
	Tonnes Yr ⁻¹	Change (%)	P-value	Tonnes Yr ⁻¹	Change (%)	P-value	Tonnes Yr ⁻¹	Change (%)	P-value
Boyne	-4.7	-3.7	<0.001	-88.6	-1.8	<0.01	-2.9	-4.2	<0.001
Tolka	-0.6	-6.0	<0.001	-9.5	4.3	<0.001	-0.2	-2.5	0.021
Liffey	-3.9	-5.6	<0.001	-33.8	-2.0	<0.001	-3.2	-5.4	<0.001
Dodder	-0.4	-4.4	<0.001	-3.5	-1.9	<0.001	-0.2	-2.6	0.019
Avoca	-1.0	-3.4	<0.01	-166.1	-4.0	<0.001	-81.0	-7.8	<0.001
Slaney	-7.4	-6.1	<0.001	-36.9	-0.6	0.087	-4.0	-5.8	<0.001
Barrow	-6.6	-4.4	<0.001	-75.6	-1.1	0.031	-3.5	-4.7	<0.001
Nore	-7.3	-4.7	<0.001	-65.4	-1.3	0.035	-3.6	-4.4	<0.001
Suir	-10.6	-5.4	<0.001	31.9	-0.5	0.503	-9.1	-4.3	<0.001
Blackwater	-18.7	-5.3	<0.001	-193.2	-2.0	<0.01	-12.3	-5.7	<0.01
Lee	-1.2	-1.5	0.124	-75.7	-2.1	<0.001	-2.1	-3.4	<0.01
Bandon	-1.0	-1.8	0.087	-48.1	-1.9	<0.001	-1.1	-2.9	0.040
Deel	-3.3	-6.1	<0.001	-25.9	-3.5	<0.001	-2.0	-5.4	<0.01
Maigue	-6.9	-5.5	<0.001	-60.9	-3.6	<0.001	-3.2	-4.9	<0.01
Shannon OC	-5.5	-4.1	<0.001	-56.8	-1.8	0.056	-3.7	-3.7	<0.01
Shannon TR	-5.9	-2.7	<0.01	-139.4	-1.6	0.011	0.7	0.6	0.673
Fergus	-0.9	-2.7	<0.01	-11.5	-1.5	0.157	-0.8	-2.0	0.014
Corrib	-0.6	-0.8	0.413	-56.6	-1.5	0.045	2.3	3.0	0.012
Moy	-1.2	-1.3	0.130	-28.7	-1.2	0.189	-0.3	-0.6	0.441
Erne	-0.3	-0.1	0.637	-51.4	-1.5	0.021	1.0	2.1	0.140

Fig. 3—Three-year (2011–13) average annual load (tonnes yr^{-1}) for (a) total phosphorus (TP), (e) total nitrogen (TN) and total ammonia (TA); three-year (2011–13) average annual export loading (kg hectare $^{-1}\text{yr}^{-1}$) for (b) TP, (f) TN and (j); percentage (%) difference between the first (1990–92) and last (2011–13) three-year average annual loads for (c) TP, (g) TN and (k) TA and the percentage difference between the maximum (peak) three-year average annual load and the last three-year average annual load for (d) TP, (h) TN and (l) TA for each of the nineteen rivers discharging to Ireland's marine environment over the period 1990–2013.

Table 7—Comparison of national direct discharges of point sources of total nitrogen (TN) and total phosphorus (TP) from wastewater and industry sources downstream of the riverine monitoring stations over two time periods. Direct discharges in monitored and unmonitored catchments are included.

Time Period	Total Nitrogen			Total Phosphorus		
	Wastewater (Tonnes $\times 10^3$)	Industrial (Tonnes $\times 10^3$)	Total (Tonnes $\times 10^3$)	Wastewater (Tonnes $\times 10^3$)	Industrial (Tonnes $\times 10^3$)	Total (Tonnes $\times 10^3$)
1986–1990	5.44	4.76	10.20	1.37	1.06	2.43
2011–2014	7.09	0.13	7.22	1.24	0.01	1.25

DIRECT DISCHARGES

A comparison of national direct discharges from wastewater and industrial point sources estimated over the period 1986–1990 and for the most recent period 2011–14 is shown in Table 7. Over the two periods, direct discharges of N have decreased by nearly a third equating to 3,000 tonnes, while discharges of P have decreased by almost a half equating to a reduction of over 1,100 tonnes. Direct discharges for both nutrients from industrial point sources have decreased dramatically from the earlier period and this probably reflects the connection of industrial discharges to the sewerage network. This is evident in the increase in the discharge of N from wastewater treatment plants in the most recent period. This is not repeated for P, which may indicate the greater net removal of TP during the wastewater treatment process. This analysis indicates that improved waste water treatment has contributed to a 50% reduction in point discharges of phosphorus to Ireland's aquatic environment. This assumes that discharges from industry have remained unchanged from the earlier period, but are now mostly being discharged to sewer.

The exercise to estimate direct discharges for the most recent period described above also provided an indication of the national breakdown between upstream and downstream point sources. For TN, upstream point sources make up 27% (2,654 tonnes) of the total load from point sources (i.e. 9,871 tonnes), while for TP, upstream sources only account for 12% (166 tonnes) of the total load from point sources (i.e. 1,422 tonnes).

DISCUSSION

This paper has demonstrated a significant decrease in river loads of the main nutrients discharging into Ireland's marine environment. This reduction is

large and statistically significant at a national, sea area and river scale. The greatest reductions have been seen in loads of TP (4,716 tonnes) and TA (5,505 tonnes) but the reduction in TN (59,396 tonnes) is also substantial, particularly in absolute terms. In the following sections we will discuss the likely causes of these reductions and their potential impact on Ireland's aquatic environment. A detailed analysis of the impact of these river nutrient reductions on a number of estuarine and coastal waters around Ireland is provided by the study of Ní Longphuirt *et al.*, which also appears in this special issue.

EFFECT OF MANAGEMENT MEASURES

The nutrient load reductions observed are substantial and while climatological factors cannot be ruled out as a possible contributory factor (Grizzetti *et al.* 2012), the magnitude of these reductions points toward the effectiveness of management measures put in place to reduce nutrient losses to the aquatic environment. These include the improvement in urban waste water treatment, changes in agricultural practices and licensing of industrial discharges. Reductions of a similar magnitude in riverine inputs as a result of mitigation measures have also been reported by other countries on the European mainland including Denmark, Germany and the Netherlands (OSPAR 2010).

In relation to wastewater treatment, Ireland has seen a marked improvement with 93.9% of the wastewater load generated in 2012 receiving at least secondary treatment (EPA, 2014). A decade earlier, only 29% of the wastewater load received at least secondary treatment, with the remaining 71% receiving only primary treatment or no treatment. While the impact of improved waste water treatment is evident in the substantial reduction in downstream direct discharges of TP, its contribution to the overall reduction in river loading of P is likely to be small. If it is assumed that upstream point source inputs of TP have decreased in the

same proportion as downstream sources (i.e. by $\sim 50\%$), then this reduction would be equivalent to the current loading of TP from upstream point sources of 166 tonnes. This would equate to $< 4\%$ of the overall reduction in riverine inputs observed over the time-series (i.e. 4,716 tonnes).

It is likely that changes in agriculture practices and in particular the reduction in the use of inorganic P fertiliser may account for the largest reduction in riverine TP loads. A source apportionment study comparing changes in nutrient sources over two periods (1995 and 2012) showed that the largest reduction in nutrient sources was from the agriculture sector (Bradley *et al.* 2015). The study showed a 37.7% reduction in P load (equating to 2,000 tonnes), which is mostly accounted for by the reduction in the use of inorganic P fertiliser following the introduction of improved farming practices and in particular the management of inorganic fertiliser application. The amount of inorganic P fertiliser usage in 2008, for example, was less than half what it was in 1995 (Lalor *et al.* 2010). The observed reduction in river loads of P of 4,716 tonnes is considerably more than can be explained by the estimated reduction from the agriculture sector of 2,000 tonnes and the assumed reduction in upstream point sources of about 166 tonnes. Furthermore, the source apportionment study referred to above indicates no substantial change in the loss of nutrients from other sources that could explain this discrepancy (Bradley *et al.* 2015). The reasons for this difference should be further examined. One possible explanation might include a continuing decline in the use of inorganic fertilizer after 2008, which would not have been captured by the source apportionment study. Another hypothesis that requires further development and testing is to examine if the reductions in P loads reported here and the associated decrease in ambient river P concentration reported by Bradley *et al.* (2015) has increased catchment nutrient retention. More specifically, have decreases in ambient P concentration been matched by a decrease in the saturation state of the various components in the environment (soil, sediment, vegetation) and if so has this increased the capacity of the river catchment to filter P before it reaches the sea?

Improved waste water treatment is likely to have made a substantial contribution to the observed reduction in TA. The greater provision of secondary treatment, even in the absence of tertiary nutrient removal, is very effective in removing ammonia through the process of nitrification. For example, when Ringsend wastewater treatment plant, the largest in the country, was upgraded from primary to secondary treatment, direct discharges of ammonia to the Liffey Estuary decreased by over 75% between 2001 and 2004 (from 2,147

to 450 tonnes) as the plant became fully operational (O'Higgins, 2006). Although the preceding example is in relation to a discharge to an estuary it can be reasonably assumed that similar reductions in ammonia discharges to inland surface waters have been achieved as the proportion of treatment plants providing secondary treatment increased over the last decade.

However, it is clear that the biggest contributor to the observed reduction in national riverine TA loads was the reduction in load from the Avoca River following the licensing and eventual closure of the Irish Fertiliser Industries plant. The difference between the maximum (4,177 tonnes) and minimum (29.7 tonnes) three-year average of 4,147 tonnes for the Avoca accounts for just over 75% of the total national reduction seen in riverine TA loads. Nevertheless, even if the Avoca is omitted, national riverine loads of TA have decreased by just under 60% and some rivers including the Suir, Deel and Maigne, have seen reductions $> 80\%$. The reduction in TA loads from riverine inputs suggest an improvement in the water quality status, and in particular a reduction in the level of organic enrichment, of these rivers. While the provision of improved waste water treatment is likely to be one of the main factors explaining the decrease in TA loads, the role of improved agricultural practices may also be significant. Indeed, this is one area where further research could help quantify the role of improved farming practices, including the management of farmyard activities, in the observed reduction in TA loads.

IMPACT ON DOWNSTREAM RECEIVING WATERS

The overall reduction in riverine inputs of nutrients reported in this paper is likely to lead to an improvement in water quality in estuarine waters. One particularly strong example of this is the improvement in the condition of the Blackwater Estuary in southern Ireland. Reductions in TP entering the estuary and MRP concentrations in the estuary have been matched by a reduction in the concentration of phytoplankton biomass and the gradual improvement in trophic status (Ní Longphuirt *et al.* 2015a). The estuary is no longer classified as eutrophic (Bradley *et al.* 2015). These improvements are likely to make a significant contribution to the achievement of the environmental objectives that have been set for this estuary under the Water Framework Directive.

The response in other estuaries to reduced river nutrient inputs may not be as linear due to differences in their sensitivity and the relative importance of P and N in limiting algal growth and the relative availability of these nutrients in the environment in question. For cell growth phytoplankton

have a requirement for N and P atoms in a ratio of 16:1, the so-called Redfield ratio (Redfield 1934). When the ratio is $>16:1$ phytoplankton growth will be limited by the availability of P, when the ratio is $<16:1$ phytoplankton growth is N limited. In freshwater systems, algal growth is usually limited by P (Vollenweider 1976; Schindler, 1977), whereas in marine influenced estuaries and coastal systems, growth is primarily limited by N (Howarth and Marino, 2006). In river-dominated estuaries in Ireland, such as the Blackwater Estuary, which are generally P limited for much of the year (N:P ratio $>100:1$ in both winter and summer) (O'Boyle *et al.* 2015), the large reduction in P loading is likely to have a significant impact on algal growth and if previously enriched a positive impact on environmental status—as was the case for the Blackwater Estuary. In contrast, in more marine-influenced estuarine systems, which are likely to be predominantly N limited, particularly in summer (Ní Longphuirt *et al.* 2015b), the more modest reductions in N load may not be sufficient to reduce algal growth. For example, in the marine-influenced Argideen Estuary, in southern Ireland, it has been estimated that reductions of more than 60% in N would be required to improve the trophic status of the estuary (Ní Longphuirt *et al.* 2015b), which is severely impacted by the excessive growth of opportunistic macroalgae. This is considerably more than the average percentage reduction of river N loads of 39% and more than the reduction that has been observed in the adjoining Bandon River catchment of 33% (direct load measurements are not available for the Argideen catchment). In such cases it is clear that further reductions, particularly of N, will be required if certain estuaries are to meet their environmental objectives set by the WFD. The varying responses of different estuaries to changes in nutrient inputs need to be fully understood if effective measures are going to be put in place to manage these valuable water resources.

What is particularly striking about the data presented here is the large reduction of total phosphorus relative to total nitrogen over the time-series—71.9% for TP versus 39.0% for TN. This probably reflects how the measures put in place to combat freshwater eutrophication have focused more on P than N as the former is considered to be the limiting nutrient in freshwater systems (Vollenweider 1976; Schindler, 1977) and that measures have been more effective in removing P than N (Grizzetti *et al.* 2012). The greater reduction in river loads of P compared to N may have important implications for the biogeochemistry and ecology of downstream receiving waters. In the upper Suir Estuary in summer, for instance, the molar inorganic ambient N:P ratio is greater than 500:1 (O'Boyle *et al.* 2015), an order of

magnitude higher than would normally be expected for undisturbed conditions. This mostly reflects the large difference in the annual load of N and P to the estuary (5,715 tonnes of N versus 71 tonnes of P), which in turn reflects the relative success of measures designed to reduce P compared to those targeting N. Phosphorus loadings, for instance, have reduced by as much as 80% from peak, whereas N loadings have only reduced by 34% from peak (this paper). Unbalanced nutrient reductions in river loadings of N and P are also likely to have contributed to the elevated inorganic molar N:P ratios ($>40:1$) observed in a number of coastal bays along Ireland's southern coast (O'Boyle *et al.* 2015).

Furthermore, related changes in the biogeochemical cycling of nutrients in downstream estuarine waters may further exacerbate the disparity in the stoichiometric nutrient ratio along the freshwater–marine gradient. For example, in a study of 14 Irish estuaries between 2000 and 2013, the reduction in riverine TP loads was matched by a comparable reduction in inorganic P concentration in the estuaries of about 60%. For N, while loads decreased more modestly by 14%, inorganic N concentrations in the estuaries remained unchanged over the period of the study (Ní Longphuirt *et al.* 2016). The reasons for this are unclear, but may be due to factors that have been observed in other estuarine areas such as a time lag between reductions in nutrient inputs and changes in estuarine concentrations due to internal nutrient loading (Cartensen *et al.* 2006), reduced biological uptake of inorganic N due to greater phosphorus limitation of algal growth (Paerl *et al.* 2004) or a reduction in the rate of denitrification due to a reduction in production of organic carbon (Cornwall *et al.* 1999).

The biological implications of elevated ambient N:P ratios on micro- and macroalgal blooms in estuarine and coastal waters is still being assessed but could include impacts on primary production and species composition of micro- and macroalgal communities. In estuarine waters, very low P levels are likely to reduce overall primary productivity and an environment rich in N compared to P (i.e. high N:P ratio) is likely to favour phytoplankton species such as mixotrophic dinoflagellates. These are capable of scavenging P from other sources, such as particulate organic matter, giving them a competitive advantage over photosynthetic dinoflagellates and other phytoplankton (Granéli *et al.* 1999). Furthermore, we suggest that favourable conditions for noxious algal blooms are created in marine-dominated estuaries (typically N limited in summer) when N rich freshwater mixes with relatively P rich seawater. This scenario might partly explain the occurrence of excessive blooms of green opportunistic attached macroalgae in a number of

marine-dominated estuaries along the southern coast of Ireland (Ní Longphuirt *et al.* 2015b). Further increases in the N:P ratio may exacerbate these events. Given the potential for this, and other possible ecological disturbances, concomitant reductions in N loads may be required in certain areas to restore the stoichiometric nutrient balance. These considerations may need only apply to estuarine and nearshore coastal areas as there is little evidence of elevated N:P ratios being present further offshore (Nolan *et al.* 2009). This is in contrast to other sea areas such as the North Sea where much larger river inputs with elevated N:P ratios result in elevated ambient N:P ratios which extend many kilometres out to sea (Burson *et al.* 2016).

CONCLUSIONS

This paper has highlighted the importance of maintaining long-term time series to detect environmental change. It has also highlighted the significant environmental change that has taken place. This change indicates that as a collective, the measures that have been put in place to reduce nutrient loss in Ireland have been effective. Nevertheless, the relative effectiveness of these different measures is still somewhat unknown. A more detailed, river catchment-scale assessment of these measures would provide further insight into their relative effectiveness and help inform the selection of future measures. Furthermore, while broadly positive, the specific nature of these changes on the biogeochemistry and ecology of inland surface waters and nearshore tidal waters needs further investigation. Further research is required to fully understand the implications of these changes on the functioning of aquatic ecosystems and their influence on the ecology and diversity of these systems. These changes need to be assessed against conditions that are considered to support the normal functioning and health of aquatic systems, and this assessment should be used to inform the effective management and protection of these resources. In particular, a holistic view along the freshwater – marine continuum must be taken to ensure that nutrient imbalances are not created in downstream coastal areas.

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