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Authors(s)	Ní Longphuirt, Sorcha, Mockler, Eva M., O'Boyle, Shane, et al.
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LINKING CHANGES IN NUTRIENT SOURCE LOAD TO ESTUARINE RESPONSES: AN IRISH PERSPECTIVE

Sorcha Ní Longphuirt, Eva M. Mockler, Shane O'Boyle, Caroline Wynne and Dagmar Brigitte Stengel

Sorcha Ní Longphuirt (corresponding author; email: s.nilongphuirt@epa.ie), Environmental Protection Agency, Inniscarra, Cork, Ireland Eva M. Mockler, UCD Dooge Centre for Water Resource Research, University College Dublin, Dublin 4, Ireland; Shane O'Boyle, European Commission, DG Environment, Beaulieu, Brussels, Belgium; Caroline Wynne, Environmental Protection Agency, Richview, Clonskeagh, Dublin 14, Ireland; and Dagmar Brigitte Stengel,Botany and Plant Science, School of Natural Sciences, Ryan Institute for Environmental, Marine and Energy Research, National University of Ireland Galway, Galway.

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ABSTRACT

In the Irish environment, anthropogenic pressures have led to widespread nutrient over-enrichment and eutrophication in surface waters. In the past 25 years European Directives have been implemented resulting in significant measures to improve water quality. Multi-decadal monitoring of nutrient inputs from rivers, and response parameters in estuarine and coastal systems, allows for a comparison of the effectiveness of these measures. In this study, trends in nutrient inputs from eighteen river systems and downstream estuarine parameters between 2000 and 2013 are explored. The results are placed in the context of changes in nutrient source load apportionment modelled through a newly developed GIS tool. Measured phosphorus inputs showed a significant reduction from fifteen catchments, with only four rivers showing a concurrent reduction in nitrogen. Significant Parallel improvements in estuarine water quality were evident in eight downstream systems, highlighting the complexity of response mechanisms. Load apportionment illustrated that the effectiveness of measures largely depended on factors such as land use and the proximity of large urban agglomerations to the estuary. The partitioning of nutrient sources could determine the nutrient landscape of the downstream estuary, with possible implications for the ecological health of the system.The results of the study will inform decision makers on the effectiveness of measures to date and the possible response of systems to future controls in the light of targets set out under the Water Framework Directive.

INTRODUCTION

Anthropogenic activities have altered global patterns of elemental cycling and increased flows of nitrogen (N) and phosphorus (P) from land to surface waters extensively in recent decades. Manifestations of nutrient enrichment are evident globally and include the occurrence of phytoplankton and opportunistic green algal blooms, decreased water quality, loss of macro benthos communities, alterations to pelagic and benthic food web structure and, in severe cases, occurrences of hypoxia (Nixon, 1998; Carstensen *et al.*, 2014;).

Estuaries are highly complex transitional systems influenced by anthropogenic pressures from terrestrial upstream catchments and also mixing with coastal zones. As such, the influence of changing human disturbance can be confounded by variability in response mechanisms relating to the level of connectivity with coastal waters and also ecosystem-specific light and hydrological conditions (Ní Longphuirt *et al.*, 2015a; O'Boyle *et al.*, 2015). The modification in the natural supply of nutrients from rivers into these transitional systems in the past few decades and the consequential degradation of surface water systems at a European level have resulted in the development of platforms, such as the European Water Framework Directive (WFD 2000/60/EC), the Marine Strategy Framework Directive (MSFD 2008/56/EC) and the Oslo-Paris Convention on the Protection of the North Eastern Atlantic (OSPAR), aimed at assessing, and setting targets for the improvement of ecological status.

In Ireland, blanket mitigation measures have been applied to reduce nutrient losses from agriculture, domestic and industrial sources (e.g. Urban Waste Water Treatment Directive (91/271/EEC), Water Quality Standards for Phosphorus Regulations 1998, Good Agricultural Practice Regulations 2005–2014, Surface Water Regulations 2009), and small-scale studies have indicated that these measures have led to a decrease in nutrient loadings to some surface water systems (Greene *et al.*, 2011; O'Dwyer *et al.*, 2013; Ní Longphuirt *et al.*, 2015b).

In the most recent WFD assessment of Irish estuarine systems (2010–12), 44.7% of the total area of transitional waters was classed at High or Good status, with a number of water bodies in the south-east and south of the country continuing to display symptoms of nutrient enrichment (Environmental Protection Agency (EPA), 2015). Currently the

EPA is rolling out an Integrated Catchment Management (ICM) approach across Ireland to assist in achieving the target of recovering all Irish water bodies to Good status (Daly 2013). This catchment-based approach is a multidisciplinary collaborative method which will allow for a focus on 'bottom-up' and 'top-down' processes and incorporates consultation with local communities and relevant public bodies to ensure a valued water resource that supports vibrant communities.

The selection of effective measures for estuarine and coastal waters will however be predicated on a well-developed understanding of (1) the effectiveness of previous measures and (2) how pressures interact with environmental factors and impact on biological receptors. This requires a multidisciplinary approach that examines the interaction between the disturbance of biogeochemical cycles, the resultant fluxes to surface water systems and the impact on biological processes (Hering *et al.*, 2015). Observational monitoring and time series are essential tools for detecting, measuring and understanding these interactions and responses. In Ireland, monitoring programmes over the past two to three decades have provided a database of information which can be synthesised to determine not only the changes in estuarine systems but also their connectivity to pollutants emanating from land-based anthropogenic activities. Furthermore, they allow for an analysis of response mechanisms and the effectiveness of national measures aimed at improving water quality, ultimately augmenting our understanding of the mechanisms that mediate ecosystem restoration (Cloern *et al.*, 2016). Linking and understanding oscillations and trends in water quality through an analysis of these parameters will in turn inform future national policy decisions and provide a background for understanding the possible implications of future scenarios of climate change and/or increased anthropogenic pressures relating to growth in population, industry or agriculture. This is particularly relevant in the context of strategic national planning such as Food Harvest 2020 and Food Wise 2025.

In this study we hypothesised that the effectiveness of blanket measures to reduce nutrient inputs to estuarine and coastal water bodies will depend on catchment characteristics including land use and the type and magnitude of anthropogenic activity. Further to this, we hypothesised that response mechanisms in estuarine systems will be dependent on localised controls such as light conditions and connectivity with adjacent marine systems.

A long-term data-driven analysis and narrative of the trends in nutrient loads from eighteen Irish catchments and the concurrent responses of downstream estuarine water bodies over a fourteen-year period (2000–13) is presented in this study. We report changes in load apportionment, trends in riverine inputs and subsequent alterations to downstream water-quality parameters (nutrients, chlorophyll). We attempt to disentangle the biophysical and chemical factors that constrain/maintain the status of Irish estuarine water bodies and identify systems where mitigation measures relating to diffuse or point sources have resulted in an improvement in water quality. The study will provide a context for identifying the nutrient sources driving water quality at national and catchment scales and therefore help inform management decisions on targeting and prioritising mitigation measures.

METHODS

SITE SELECTION AND METHODOLOGY

Nutrient inputs from eighteen of the major rivers in Ireland have been monitored monthly since 1990 to determine discharges to the maritime area in accordance with the objectives of the OSPAR Riverine Inputs and Direct Discharges (RIDD) programme (Fig. 1). As such, the position of these sites determined the scope of the catchments analysed and the associated downstream estuarine systems investigated in this study. Measured riverine inputs from the monitored rivers were analysed for temporal trends from 2000 to 2013 (see also O'Boyle *et al.*, 2016). A source load apportionment model (LAM) was also run for each catchment for 2000 and 2013 and compared to the riverine inputs. Through the model outputs, changes in load apportionment from different sectors (diffuse and direct) in each system were identified. Loads were determined for the catchment area both upstream and downstream of the sampling stations used to collect data for riverine inputs. Downstream of the eighteen river stations the estuarine systems were split into seventeen mesohaline (0–17 salinity), sixteen polyhaline (17–30 salinity) and thirteen mixoeuhaline (>30 salinity) water bodies for the purpose of analysing trends in response parameters (nutrients, chlorophyll). These distinctions in water body differ, albeit only slightly, from the water-body delineations considered for reporting under the WFD. Trends were then reviewed in the context of reductions in nutrient loads where appropriate. Estuarine responses to reduced upstream nutrient loads are discussed and considered in the context of the drivers of ecosystem health, the effectiveness of national measures aimed at improving water quality, and the factors that may mitigate or deflect biological responses.

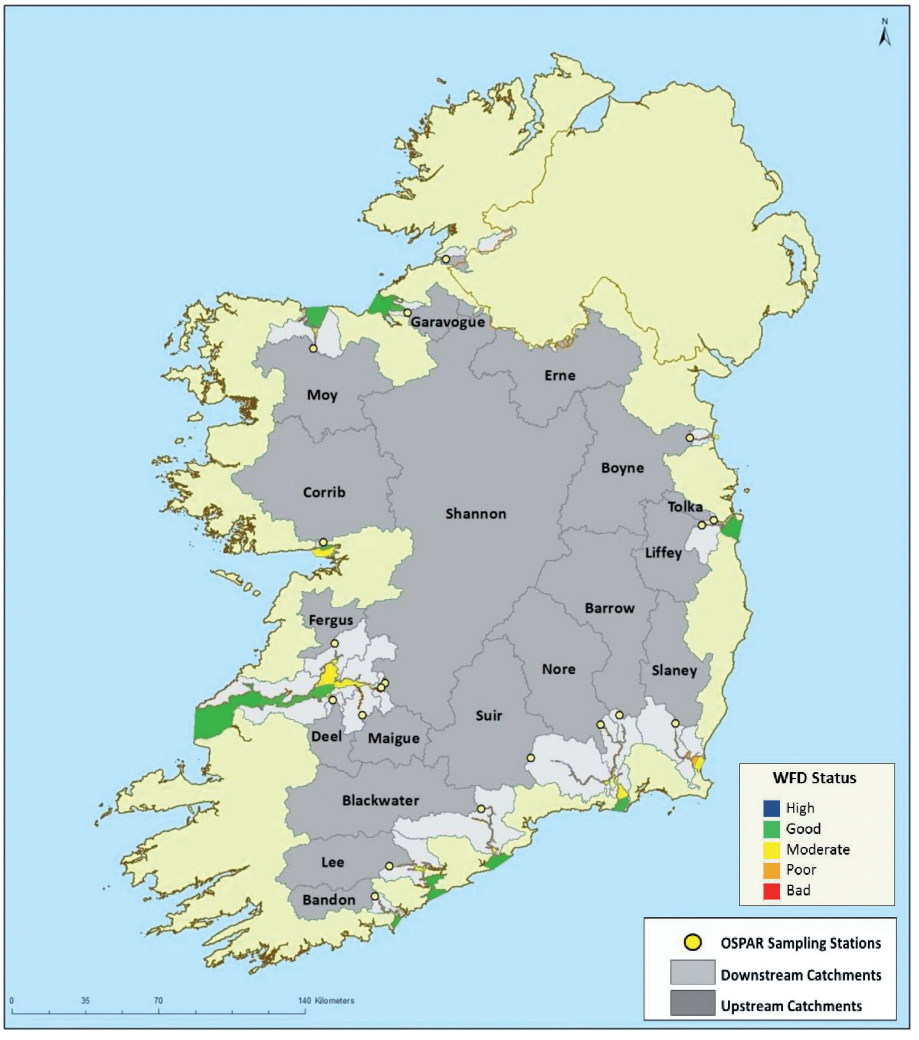


Fig. 1—Map of Ireland with the upstream (dark grey) and downstream (light grey) catchments analysed within the scope of the study. Yellow dots represent the monitoring stations where riverine nutrient inputs and flows were sampled. Water Framework Directive Status (2010–12) for the receiving transitional and coastal waters is also displayed.

NORMALISED RIVERINE NUTRIENT INPUTS

Monthly water samples were collected from the eighteen rivers and analysed to give nutrient concentration data (mg L^{-1}) for total phosphorus (TP), unfiltered molybdate reactive phosphorus (MRP), total nitrogen (TN), total oxidised nitrogen (TON) and ammonium (NH_4^+). Nutrients were measured according to Standard Methods for the Examination of Water and Wastewater (2005) (www.standardmethods.org).

The individual concentration of each specific nutrient transported by a river was first multiplied by its corresponding flow. These were then summed annually and divided by the sum of the flows in each year. This was considered the flow weighted mean concentration (FWMC, mg m^{-3}) and can be expressed by:

$$\mathrm{FWMC} = \frac{\Sigma_{i=1}^{n}(C_i Q_i)}{\Sigma_{i=1}^{n}(Q_i)} \tag{1}$$

where Ci is the concentration measured in sample i (mg m^{-3}); Qi is the corresponding flow for sample i (m^3 s^{-1}); and n is the number of samples taken in the sampling period (year).

The annual flow normalised input (t yr^{-1}) for each parameter was then calculated by multiplying the FWMC by the annual flow (Q_r, m^3 yr^{-1}) for each river and dividing by an annual flow normalisation factor ($Norm_f$) to remove the effects of oscillations in flow and hence rainfall/weather and allow comparability with the load source apportionment:

$$\text{Annual flow normalised input} = \frac{FWMCxQ_r}{Norm_f}. \tag{2}$$

The normalisation factor is calculated as the long-term average flow (Q_{LTA}) divided by the annual flow for each year. The nutrient inputs presented are hence a flow-normalised input.

SOURCE LOAD APPORTIONMENT MODELLING

Nutrient load apportionment was determined for the eighteen catchments in Ireland in 2000 and 2013 to identify changes in load source over the period. A GIS-based model was used for both years. The model used for each year was data-driven and dependent on the best available dataset for that year. The 2000 dataset was much less comprehensive, particularly for industrial and domestic wastewater treatment sources, and as such the methods used to estimate load apportionment during this period were based specifically on the methods outlined in Ní Longphuirt *et al.* (2015a). For the 2013 dataset a more extensive analysis was possible and thus the methods are those detailed in Mockler *et al.* (2016). A detailed account of load calculations for diffuse (inorganic and organic fertiliser, land use, unsewered population) and point (wastewater treatment plants, industry) sources of nutrients has been provided in these two studies. The 2013 model was validated for upstream loads to an average of 10% of measured loads for TP and 4% of measured loads for TN. Due to the differences in model procedures between 2000 and 2013, load apportionment results are discussed in terms of relative changes in diffuse and point nutrient sources to estuarine surface waters.

ESTUARINE MONITORING DATA

The EPA has been monitoring Irish estuarine systems on a seasonal winter/summer basis since the 1980s. A number of monitoring sites in each of the estuaries were sampled once during winter and three times during the productive period between May and September. Samples for the analysis of chlorophyll and nutrients were collected using a 2 L Hydrobios Ruttner bottle at the surface and 0.5m above the bottom. Dissolved oxygen saturation (DO Sat) together with temperature, salinity and depth were recorded using a Hydrolab datasonde conductivity, temperature and depth (CTD) sensor. For practical purposes tidal sampling was scheduled to take place in mid- to late morning (8.00–11.00 a.m.) and again in mid- to late afternoon (2.00–5.00 p.m.) to capture tidal variation. Samples for the measurement of chlorophyll, a proxy for phytoplankton biomass, were filtered using Whatman GF/C glass fibre filters and stored overnight in the dark to prevent photo-degradation. Pigments were extracted using hot methanol and absorbance (not corrected for the presence of phaeopigments) was measured using a spectrophotometer (Standing Committee of Analysts, 1980). Ammonium (NH_4^+), total oxidised nitrogen (TON) and unfiltered molybdate reactive phosphorus (MRP) were measured according to Standard Methods for the Examination of Water and Wastewater (2005). Water transparency at each station was measured using a 25cm diameter Secchi disc.

STATISTICAL TREND ANALYSIS

Statistical analyses of temporal trends in both riverine inputs and physicochemical parameters in each estuary were undertaken using non-parametric seasonal Mann–Kendall tests (Hirsch *et al.*, 1991) using the R platform and the TTA trend analysis package (Devreker and Lefebvre, 2014). The riverine input data were analysed as an overall annual trend. However, this tool also allows the identification of temporal trends while taking into consideration seasonal variations, and will thus consider the trend within months (e.g. all data in January) before combining the trends to give an overall annual trend. In the case of the estuarine data, seasonal trends were analysed in this manner for each of the parameters tested to account for the relative importance of seasonality and weather conditions (e.g. storm events and rainfall) on nutrient concentration in the estuary. All trends were considered significant at a P value lower than 0.05.

RESULTS

SOURCE LOAD APPORTIONMENT MODEL

Considering all catchments together, N emanated mainly from diffuse sources in both 2000 (90%) and 2013 (92%) (Fig. 2). Catchments with large urban agglomerations (e.g. Liffey) did however exhibit a lesser importance of diffuse N sources. In contrast, diffuse sources represented a lesser 58% (2000) and 70% (2013) of all P entering estuarine waters. There was a large variability in the importance of diffuse P to individual estuarine systems in 2000, with diffuse sources ranging from 5% to 92% of all P sources (Fig. 2). In 2013 the importance of diffuse P sources rose in most systems, reflecting the magnitude decrease in point sources of P, which surpassed that of diffuse sources. Catchments with high point P sources were, in general, linked to large agglomerations as observed for N (Fig. 2).

The separation between upstream and downstream sources highlighted the importance of nutrient transport from the catchment directly surrounding the estuarine system (Fig. 2). Specifically in the case of point sources, downstream sources made up a large proportion of the load due

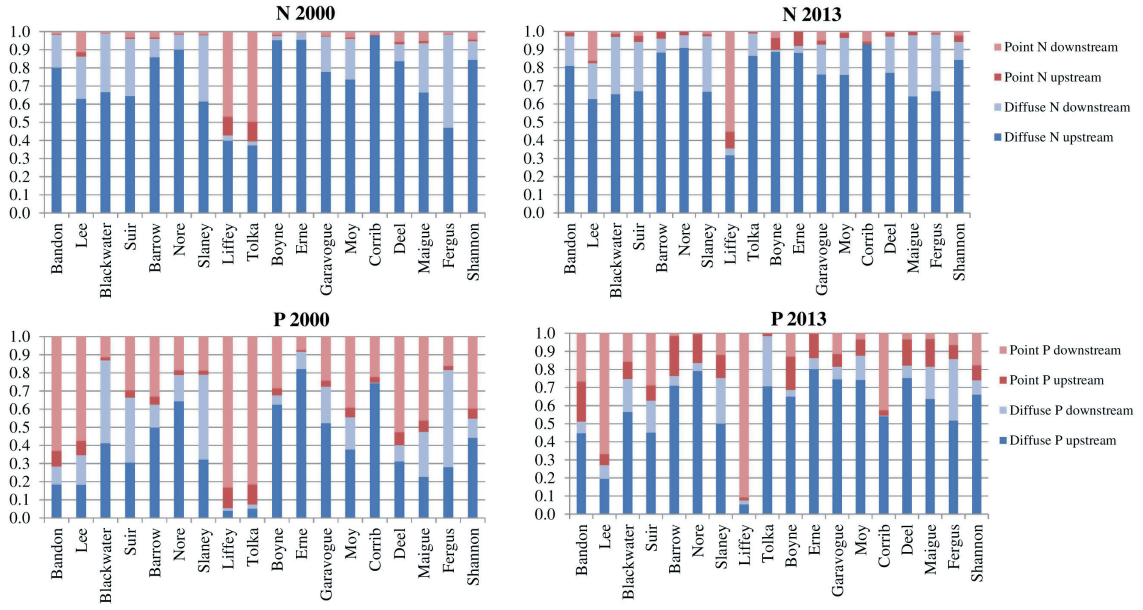


Fig. 2—Calculated nutrient load source apportionment percentage contribution for the 18 catchments studied. Point N and P relate to point sources of nutrients (wastewater treatment plants and industry) entering the estuarine system. Diffuse N and P relate to sources from agriculture, septic tanks, runoff and atmospheric deposition. Upstream sources are those above the station where riverine nutrient inputs to transitional and coastal systems are calculated (above zero salinity); downstream sources refer to those below this point (see Fig. 1).

to the location of large agglomerations and industry close to the river mouth (e.g. Liffey, Lee, Tolka). In the case of diffuse sources the relative influence of downstream sources was often dependent on the size of the catchment upstream and downstream and the length of the estuarine system.

The LAM model indicated that loads of N and P from point sources decreased by 7% and 5% respectively from 2000 to 2013 for all the catchments combined. Concurrently, modelled diffuse source loads of N and P decreased by 30% and 37% respectively. On average agriculture represented 94% and 89% of the diffuse N load in 2000 and 2013 respectively, and was split between pasture (95%: 2000, 88%: 2013) and arable (5%: 2000, 12%: 2013) land. In the case of P the importance of agriculture to diffuse sources was lower than for N at 63% and 59% respectively in 2000 and 2013. However, the relative amounts from pasture (90%) and arable (10%) land were equal for the two years. The importance of loads from waste water treatment plants (WWTPs) to point sources remained stable for N and P from both 2000 and 2013 (78%–86%), reflecting the stable ratio between wastewater from domestic and industrial sources and the concurrent decrease in both sectors in the ten-year period.

The LAM indicated that the relative importance of different load sources to (a) the overall load and (b) the load reduction was dependent on the individual catchment. For example, while reductions in P in the Bandon were largely attributed to point sources (industrial) the overall greatest contributor to P load in the upstream Bandon catchment in 2013 was agricultural sources. In contrast, the reduction in P loads in the Blackwater was driven by diffuse agricultural sources which were also the main source of P in the catchment. These differences, highlighted in Table 1 and Fig. 3, are indicative of the diversity of load sources for each catchment.

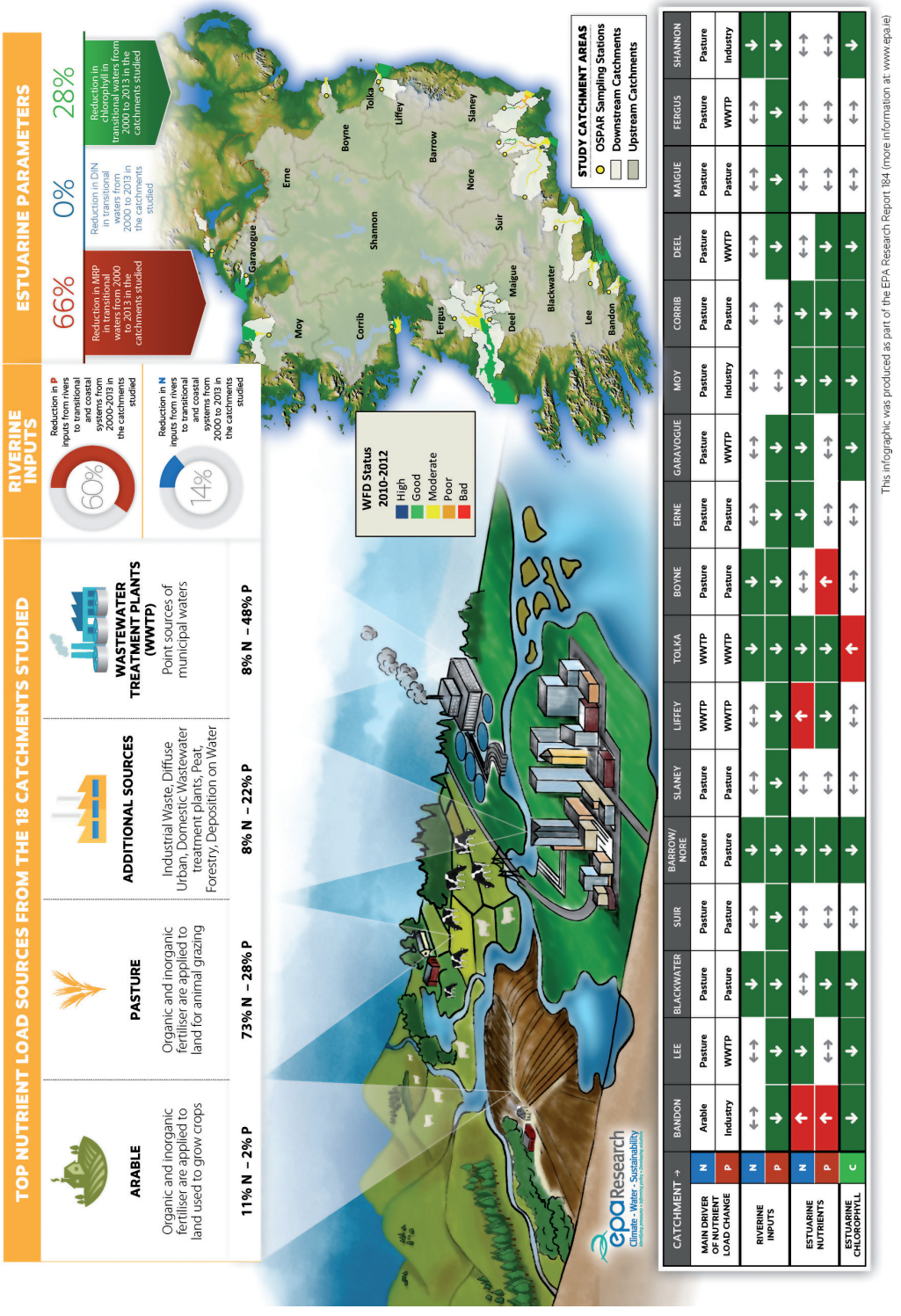
Agriculture was identified as the main driver of N load changes in all but two of the catchments studied (Fig. 3; Table 1). N load reductions were effected mainly by reductions in fertiliser applications to pasture. In the case of three catchments, increases in fertiliser application to pasture (Fergus) or both arable and pasture land use types (Bandon and Lee) drove the overall increase in N loads (Table 1). In the Liffey and Tolka catchments N and P load reductions were driven by improvements in wastewater treatment and reflect the large agglomeration of Dublin situated in these catchments.

In the case of P, load changes were driven by point source reductions in 10 catchments and agriculture (pasture) in eight catchments (Fig. 2 and 3). These results are reflective of the overall importance of point source P loads to overall P entering Irish estuarine systems in Ireland. The Tolka catchment shows an almost complete removal of point source loads, indicating changes in the wastewater treatment in this catchment over the fourteen-year time frame.

Table 1—Synopsis of the trends in load apportionment (not statistically tested) for each catchment.

	Load apportionment model trends:% change in source (change relative to overall model change is shown in parentheses)							
Catchment	*N 2013 greatest contributor*	*Overall decrease*	*N diffuse*	*N point*	*P 2013 greatest contributor*	*Overall decrease*	*P diffuse*	*P point*
Bandon	Diffuse upstream	12%	**11% (90%)**	73% (10%)	Diffuse upstream	−76%	−56% (−21%)	**−83% (−79%)**
Lee	Diffuse upstream	17%	**11% (59%)**	48% (41%)	Point downstream	−39	−52% (−47%)	**−31% (−53%)**
Blackwater	Diffuse upstream	−17%	**−19% (−100%)**	161%	Diffuse upstream	−48%	**−55% (−100%)**	2%
Suir	Diffuse upstream	−23%	**−24% (−100%)**	13%	Diffuse upstream	−53%	**−55% (−70%)**	−48% (−30%)
Barrow	Diffuse upstream	−11%	**−11% (−96%)**	−11% (−4%)	Diffuse upstream	−52%	**−41% (−50%)**	**−67% (−50%)**
Nore	Diffuse upstream	−24%	**−25% (−100%)**	−2%	Diffuse upstream	−43%	**−40% (−73%)**	−56% (−27%)
Slaney	Diffuse upstream	−20%	**−21% (−100%)**	12%	Diffuse upstream	−61%	**−63% (−81%)**	−54% (−19%)
Liffey	Point downstream	−20%	**−34% (−72%)**	−10% (−28%)	Diffuse upstream	−37%	−12% (2%)	**−39% (−98%)**
Tolka	Diffuse upstream	−86%	−64% (−30%)	**−100% (−70%)**	Diffuse upstream	−92%	0%	**−100% (−100%)**
Boyne	Diffuse upstream	−33%	**−39% (−100%)**	199%	Diffuse upstream	−41%	**−40% (−66%)**	−43% (−34%)
Erne	Diffuse upstream	−73%	**−75% (−100%)**	209%	Diffuse upstream	−94%	**−5% (100%)**	64%
Garavogue	Diffuse upstream	−57%	**−59% (−100%)**	13%	Diffuse upstream	−19%	−4% (−18%)	**−43% (−82%)**
Moy	Diffuse upstream	−51%	**−50% (−96%)**	−56% (−4%)	Diffuse upstream	−55%	−25% (−27%)	**−87% (−73%)**
Corrib	Diffuse upstream	−27%	**−26% (100%)**	149%	Diffuse upstream	−42%	−19% (−100%)	100%
Deel	Diffuse upstream	−26%	**−23% (−82%)**	−70% (−18%)	Diffuse upstream	−65%	−27% (−17%)	**−89% (−83%)**
Maigue	Diffuse upstream	−24%	**−21% (−82%)**	−76% (−9%)	Diffuse upstream	−74%	−55% (−35%)	**−91% (−65%)**
Fergus	Diffuse upstream	28%	**30% (99%)**	15% (1%)	Diffuse upstream	−40%	**−35% (−75%)**	−53% (−25%)
Shannon	Diffuse upstream	v42%	**−44% (96%)**	−37% (−4%)	Diffuse upstream	−55%	−27% (−32%)	**−69% (−68%)**

Values in bold type have the greatest impact on overall nutrient reduction.



CATCHMENT →		BANDON	LEE	BLACKWATER	SUIR	BARROW/ NORE	SLANEY	LIFFEY	TOLKA	BOYNE	ERNE	GARAVOGUE	MOY	CORRIB	DEEL	MAIGUE	FERGUS	SHANNON
MAIN DRIVER OF NUTRIENT LOAD CHANGE	N	Arable	Pasture	Pasture	Pasture	Pasture	Pasture	WWTP	WWTP	Pasture	Pasture	Pasture	Pasture	Pasture	Pasture	Pasture	Pasture	Pasture
	P	Industry	WWTP	Pasture	Pasture	Pasture	Pasture	WWTP	WWTP	Pasture	Pasture	WWTP	Industry	Pasture	WWTP	Pasture	WWTP	Industry
RIVERINE INPUTS	N	↔	↔	↔	↔	↔	↔	↔	↔	↔	↔	↔	↔	↔	↔	↔	↔	↔
	P	↔	↔	↔	↔	↔	↔	↔	↔	↔	↔	↔	↔	↔	↔	↔	↔	↔
ESTUARINE NUTRIENTS	N	↑	↔	↔	↔	↔	↔	↑	↔	↔	↔	↔	↔	↔	↔	↔	↔	↔
	P	↑	↔	↔	↔	↔	↔	↔	↔	↑	↔	↔	↔	↔	↔	↔	↔	↔
ESTUARINE CHLOROPHYLL	C	↔	↔	↔	↔	↔	↔	↔	↔	↑	↔	↔	↔	↔	↔	↔	↔	↔

Fig. 3—Graphical summary. The top section details the combined sources of nutrient loads for the eighteen Irish catchments studied, as identified through load apportionment modelling, and the measured reduction in riverine inputs and the corresponding changes in estuarine parameters between 2000 and 2013. The table at the bottom identifies the changes that have occurred in each individual estuarine and coastal system, and the corresponding drivers of nutrient change.

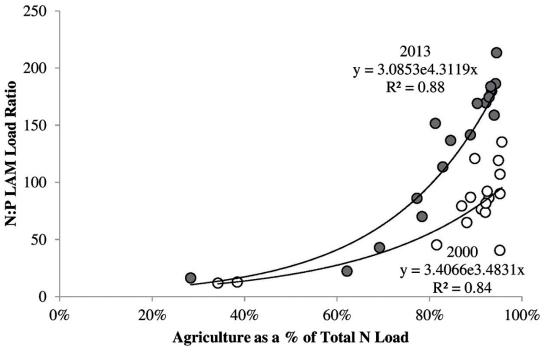


Fig. 4—Relationship between the importance of agriculture to the overall load of the catchment and the N:P load ratio as determined by the LAM model. Grey dots represent 2013; white dots represent 2000.

The N:P ratio of the LAM for all catchments (with the exception of the Garavogue) increased from 2000 to 2013, with average ratios of 35.2 in 2000 and 58.9 in 2013. An analysis of the data indicated that for both 2000 and 2013 the N:P load ratio was strongly linked to the importance of agriculture to the total N load in the eighteen catchments (Fig. 4). The relationship between these two factors changed between 2000 and 2013, reflecting the higher N:P load emanating from agriculture in 2013 (Table 2). No link was found between N:P load ratios and P loads, suggesting that the agricultural N load apportionment was the driving factor behind the N:P ratios of nutrient loads. Reductions (or increases in the case Cork and Bandon) in LAM N loadings are mainly due to diffuse source load oscillations (Table 1).

NORMALISED RIVERINE INPUTS

Nationally, normalised measured nutrient inputs to estuarine systems from upstream rivers have significantly decreased in the period from 2000 to 2013 (Fig. 5–7). The large reductions in P calculated by the LAM (Table 1) are matched by reductions in riverine inputs of P (TP or MRP) in fifteen of the eighteen catchments studied, and most rivers showed consistent decreases in TP and MRP from 2005 onwards (Fig. 5). In the systems showing a significant trend, the reductions resulted in a 48% decrease in TP in the fourteen-year period of study (considering an average of data from 2000–02 and 2011–13). The largest significant decreases in normalised TP and MRP inputs (kg P km^{-2} yr^{-1}) were recorded for the Maigue Estuary followed by the neighbouring Deel, the Tolka and the Blackwater. Two systems (Moy and Corrib) do not show any significant decrease in either TP or MRP inputs.

Table 2—Molar nitrogen to phosphorus ratios for nutrients emanating from agriculture, wastewater treatment plants and industrial waste.

Sector	*N:P 2000*	*N:P 2013*
Agriculture	170 ± 92	289 ± 189
WWTP	10 ± 4	23 ± 15
Industrial waste	10 ± 7	44 ± 65

Reductions in riverine N inputs were identified in only four of the catchments studied, with improvements again in evidence from *c.*2005 onwards in a number of systems (Fig. 6 and 7). Within these four, the average decrease in TN was approximately half of that observed for MRP (24%). Reductions in N inputs were always associated with concurrent improvements in P inputs. Significant reductions in NH_3 inputs were evident in six systems and were an indication of reductions in organic sources of N to the system (Fig. 6) (see O'Boyle *et al.*, 2016 for further analysis). As a result of the disparity between the N and P inputs there has been a statistically significant increase in TN–TP and/or MRP–TON input ratios in five of the catchments studied (Fig. 7).

ESTUARINE PARAMETERS

The response to reducing P riverine inputs was almost immediate in eight of the estuarine systems, with significant decreases in estuarine MRP corresponding to decreases in upstream inputs and concentrations (Fig. 8; Table 1). However two further systems showed a decrease in estuarine MRP without a corresponding reduction in inputs (Moy, Corrib), indicating the importance of downstream point source inputs to these estuarine systems. Two systems (Bandon and Boyne) exhibited increases in MRP concentrations in the polyhaline areas of the system. In both cases inputs of MRP from the upstream river had decreased, and this again indicates the probable importance of more localised sources of P influencing the nutrient trends (Table 1). Of the estuarine systems encompassed by this study, only four are at Moderate status as a result of high MRP concentrations and of these, three (Liffey, Tolka, Deel) show significant decreasing MRP trends, while one (Maigue) exhibits a non-significant decreasing trend.

Only six estuaries showed a decreasing trend in dissolved inorganic nitrogen (DIN), with two (Liffey, Bandon) exhibiting increases. Decreasing N inputs and linked improvements in the downstream estuary were in evidence for only one system, the Tolka. The Blackwater, Boyne, Barrow–Nore and Shannon displayed no significant change in estuarine conditions even with a decrease in riverine N inputs, highlighting the complexity of nutrient cycling in estuarine systems (Table 2).

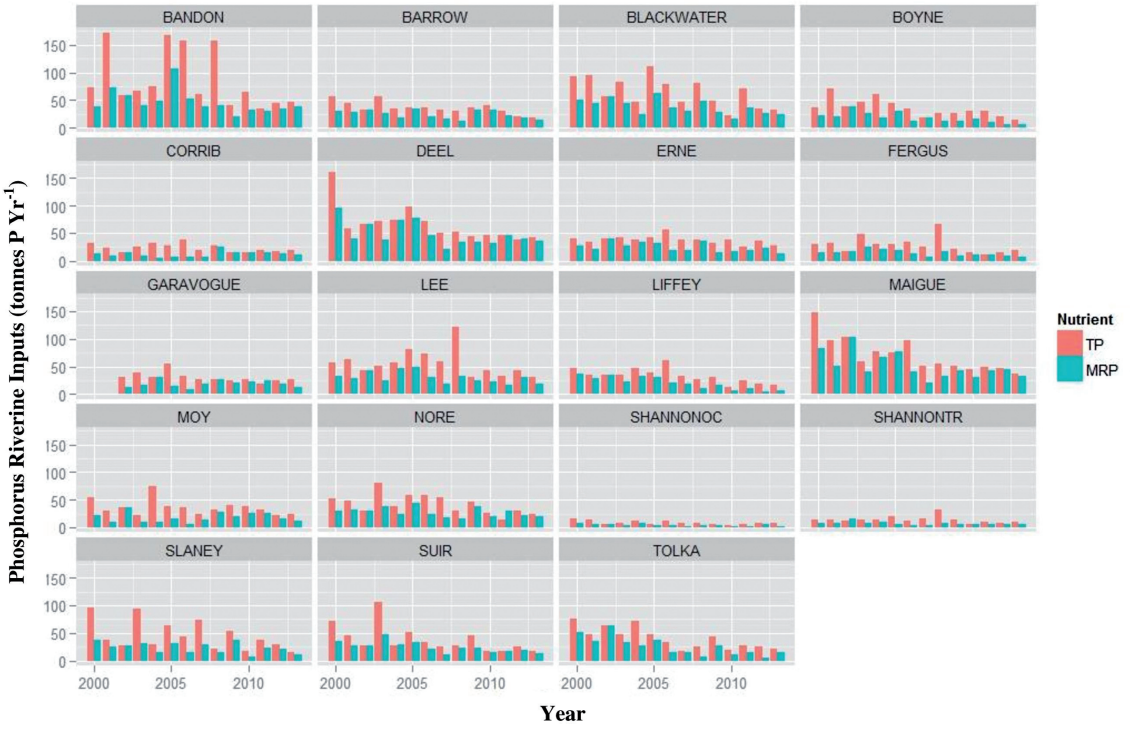


Fig. 5—Annual flow normalised total phosphorus (TP) and molybdate reactive phosphorus (MRP) exported downstream from the eighteen riverine systems to transitional and coastal areas between 2000 and 2013. Nutrient inputs for the Shannon are measured at Ardnacrusha and the Parteen Weir; as the river is split into two sections at this point these are reported as Shannon OC and Shannon TR respectively.

While not considered in the final WFD classification of water bodies under 30 salinity, five out of seventeen of the systems had DIN concentrations considered to be above the Good–Moderate status boundary (Surface Water Regulations, S.I. 272 of 2009). Of these, the Liffey and Bandon both exhibited increases in DIN. The LAM for the Bandon catchment indicated an increase in N loads

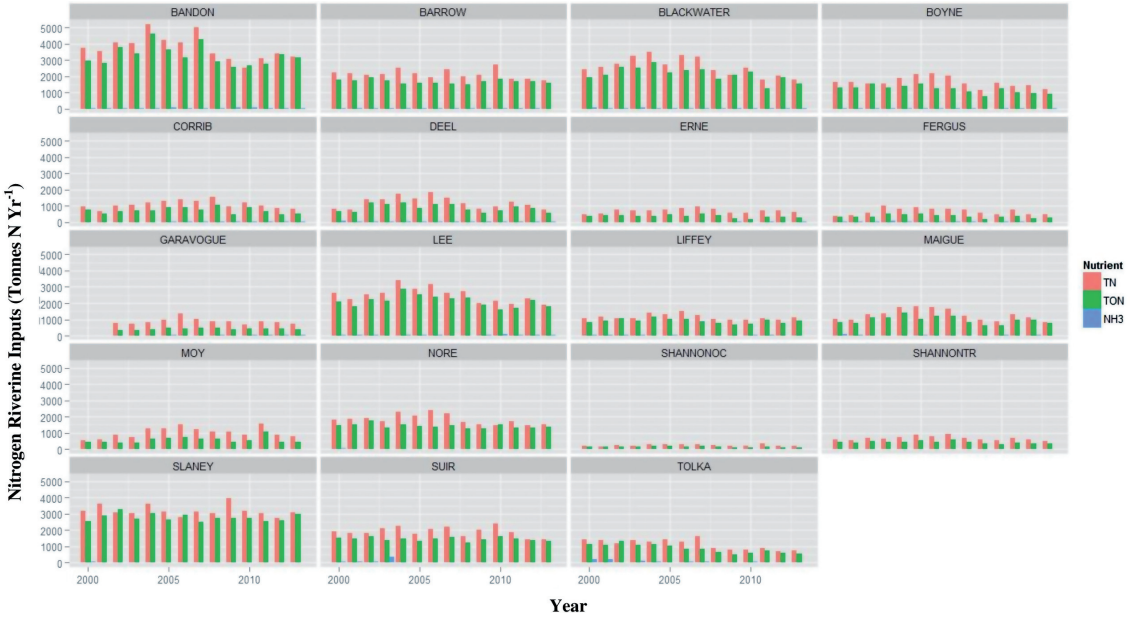


Fig. 6—Annual flow normalised total nitrogen (TN), total oxidised nitrogen (TON) and ammonium (NH_3) exported downstream from the eighteen riverine systems to transitional and coastal areas between 2000 and 2013.

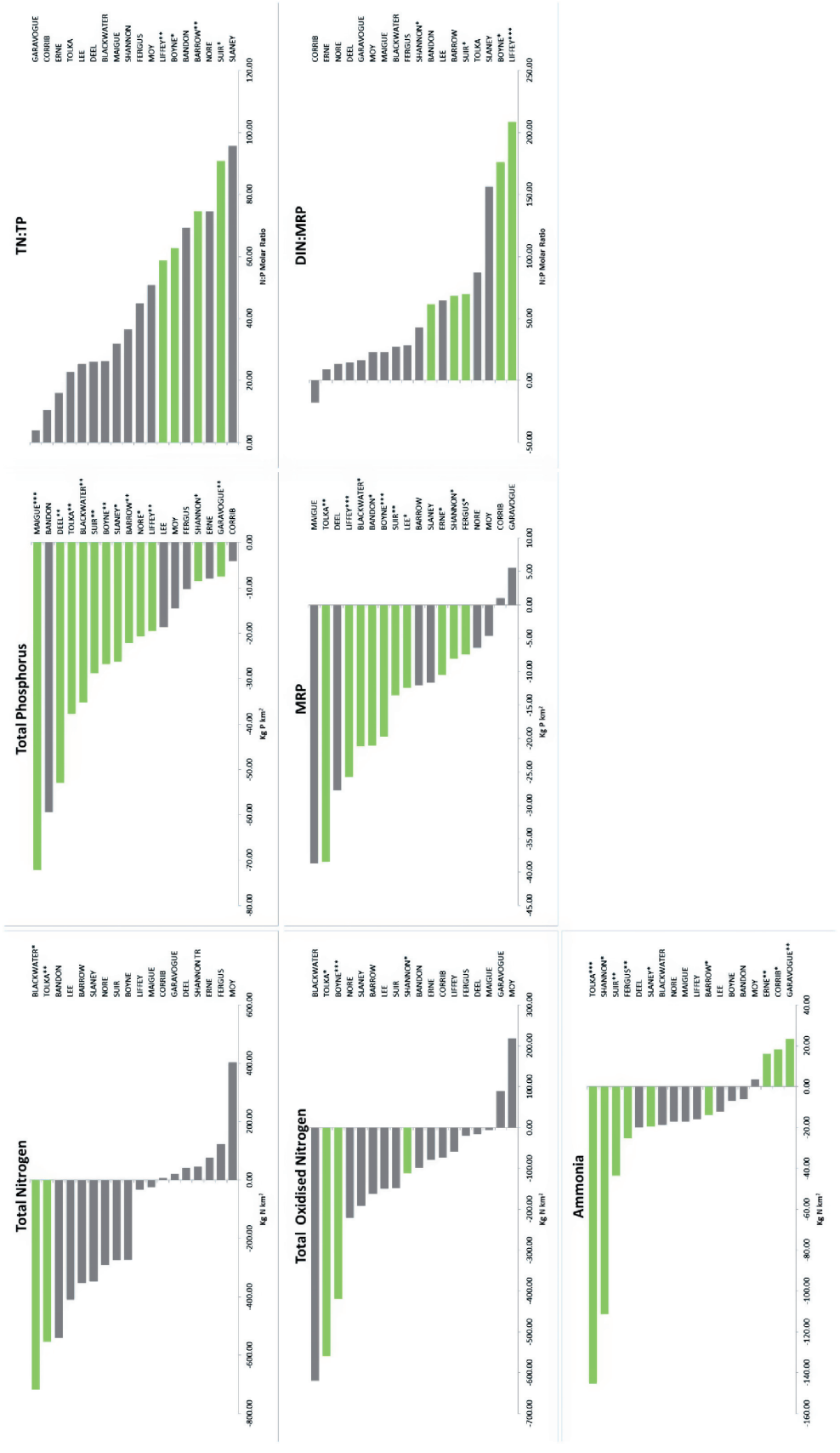


Fig. 7—Normalised differences in riverine nutrient inputs between 2000–02 and 2011–13 in the eighteen catchments studied. Green bars represent reductions found to be statistically significant (Mann Kendall trend analysis); the level of significance is denoted after the catchment name (*$P < 0.05$, **$P < 0.01$, ***$P < 0.001$).

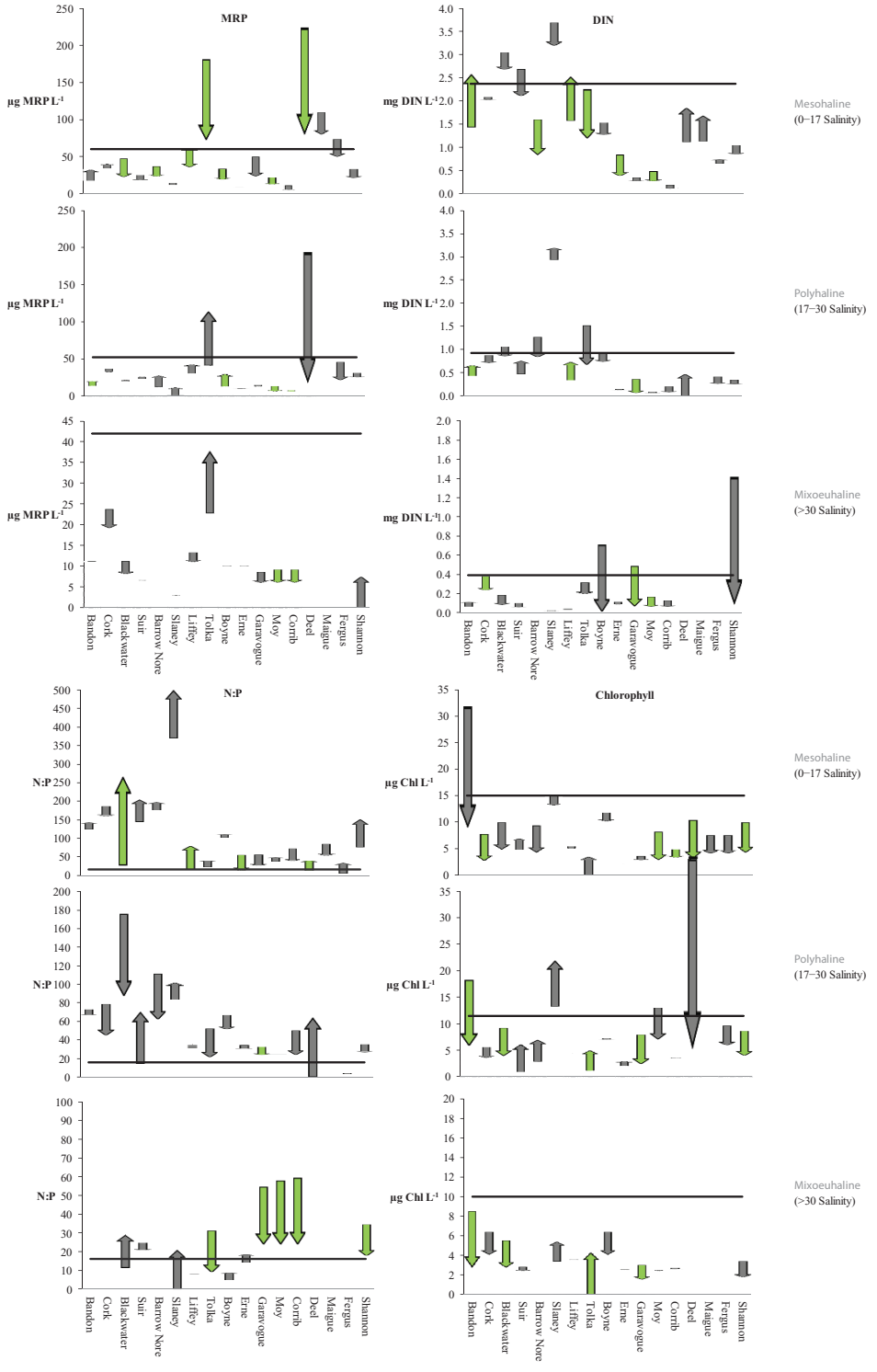


Fig. 8—Trajectories of concentrations in nutrient parameters as calculated by the Sen estimator (R TTA tool) from 2000 to actual concentrations (median summer 2011–13). Green arrows represent statistically significant trends. Solid black lines represent the EPA's Good–Moderate boundary for MRP, DIN and chlorophyll. These boundary values are based on S.I. 272 of 2009 but are salinity-dependent and hence represent average values for each of the salinity bands considered. Note: Each water body was split into three salinity bands for the purpose of the trend analysis: mesohaline (0–17), polyhaline (17–30) and mixoeuhaline (>30). If a water body is not represented in one of the graphs (e.g. Maigue mixoeuhaline) it means there were no stations in this salinity band. There is a difference in scale in the *y*-axis between the salinity bands in some cases.

which was largely driven by increases in N emanating from arable land. This may have impacted on the concentration in this estuary along with nutrient-cycling processes as detailed in the discussion below.

Summer molar ratios of N to P were on average above the Redfield ratio of 16 (Redfield, 1934) in the majority of systems studied (Fig. 8). This indicated that, in general, P was the limiting nutrient in most systems during the summer period. In the mixoeuhaline sections of the Liffey, Boyne, Tolka, Shannon and Erne, the polyhaline section of the Fergus and the mesohaline section of the Erne and Boyne, average N:P molar values of below 20 were determined. This suggested that N limitation was prevalent in these areas. An analysis of trends in N:P molar ratios indicated that between 2000 and 2013 reductions were evident in six estuaries, with a further three exhibiting increases in the mesohaline section. Estuarine chlorophyll concentrations decreased in eight of the estuarine systems studied, and can be linked, in most cases, to decreases in N or P influxes and/or concentrations (Table 1). Only 1 system (Tolka) showed a significant increase in chlorophyll.

DISCUSSION

THE ROLE OF POLICY IN REDUCING NUTRIENT INPUTS TO ESTUARINE AND COASTAL SYSTEMS

The effectiveness of policies and measures enacted to improve water quality can only be assessed by monitoring programmes undertaken after they have been implemented. The striking and significant reduction in riverine nutrient inputs in the majority of catchments studied and the concurrent improvement in estuarine concentrations is hence an indication of the success of policies implemented to reduce nutrient inputs over the past two decades.

A larger and more widespread decrease in P relative to N nutrient reductions was evident from the LAM, riverine inputs and the estuarine data sets (Fig. 3, 7 and 8; Table 1). These results suggest that mitigation measures that have focused more on P reductions have been effective (O'Boyle *et al.*, 2016).

Broad-scale reductions in diffuse agricultural loadings have had a large influence on the load reductions observed (Fig. 3 and 7; Table 1). Grassland-based dairy and mixed livestock comprise 90% of utilised agricultural land in Ireland (which represents 56% of total land use) (Wall *et al.*, 2011) and, as a result, the implications of inorganic fertiliser reduction measures can be considered a key reason for the observation of large nutrient load reductions highlighted on a national scale. The Water Quality Standards for Phosphorus Regulations 1998 led to the introduction of nutrient management planning as part of a suite of measures required to maintain or improve water quality. These measures were applied at a national level and so were applied to all agricultural lands. Agricultural application rates of P were limited to replacement values which consider soil available P (Morgan's soil test) and hence provided a targeted approach resulting in a more than 50% reduction in phosphorus fertiliser use from 1995 to 2008 (Wall *et al.*, 2011).

The Good Agricultural Practice regulations (2005) and later modifications came into effect on 1 February 2006, and were a key management strategy in Ireland's implementation of the Nitrates Directive (1991, 91/676/EEC). These regulations were the first to limit the magnitude, application, timing, rates, storage and placement of inorganic fertilisers and organic manures containing both N and P (Taylor *et al.*, 2012). Nationally, N is set at an organic loading cap of 170kg organic N ha^{-1} yr^{-1} (with a derogation possible to 250kg organic N $ha^{-1}yr^{-1}$), with inorganic application rates calculated to ensure a maximum that does not surpass a total of 226 kg N $ha^{-1}yr^{-1}$. These regulations limit not only organic N but, by association, organic P application rates.

The LAM data indicated that N:P load ratios emanating from agriculture have increased since 2010. This can be related to national trends towards a reliance on high N fertiliser compounds rather than high P and potassium (K) compounds, while the use of straight N fertiliser has also increased (Lalor *et al.*, 2010). Consequently, a relatively larger decrease in the usage of P and K than that of N has been observed. A survey of Irish farms has outlined that N usage for grassland increased from 1995 but decreased steadily from 1999 to 2008, broadly in line with changes in the national N fertiliser consumption, while for P and K steady reductions in sales and usage have been apparent from 1995 (Lalor *et al.*, 2010).

Further national measures that have reduced nutrient transport to surface water but are, as yet, not covered in the LAM include minimum requirements for on-farm infrastructure for slurry and manure storage, and housing facilities. A closed period for the spreading of organic and inorganic fertiliser during the high rainfall season (15 September to 31 January) has reduced the incidental loss of organic and inorganic fertilisers and has been shown to limit impact of agricultural wastes on water quality during these periods (Flynn *et al.*, 2016). Indeed, this major control of winter application rates was reflected in the trend analysis of river inputs to the Blackwater Estuary, where annual trends were largely driven by winter decreases in N and P (Ní Longphuirt *et al.*, 2015a).

In the case of P, the voluntary phase-out of the use of phosphate-based detergents by the Irish Cosmetics and Detergents Association (ICDA) between 1999 and 2005 is also not captured in the LAM calculations but will have had a significant impact on river inputs.

The decreased importance of point P sources in the LAM from 2000 to 2013 indicates the large impact of improved treatment and control in WWTPs and the industrial sector in this time frame. Indeed while 30% of wastewater received no treatment in 2001, this figure was down to 5% in 2014; wastewater receiving secondary (biological) treatment improved from 29% to 94% in the same timeframe (EPA, 2014) (see O'Boyle *et al.*, 2016, for additional information). Improvements in wastewater treatment have been undertaken nationally since the implementation of the Urban Waste Water Treatment Directive in 1991 through the Urban Waste Water Treatment Regulations 2001–10. A further national measure to prevent and reduce pollution by urban wastewater discharges was the introduction in 2007 of a licensing and authorisation process for such discharges.

NUTRIENT RESPONSE TIMING AND DIRECTION: THE IMPORTANCE OF NUTRIENT CYCLING AND MITIGATION FACTORS

The links between decreased N loads and the response of riverine inputs and estuarine systems are extremely variable (Table 1) and highlight the complexity of recovery trajectories in estuarine and marine ecosystems (Duarte *et al.*, 2009; 2015; Ní Longphuirt *et al.*, 2015a). Overall reductions in P, calculated from the LAM or the riverine inputs, are much greater than N, and the downstream MRP responses within the timeframe of the study are, in general, significant. The inconsistent responses of some estuarine systems to nutrient load oscillations can be the result of a number of processes.

While nutrient limitation can differ along the river–estuary continuum, in the majority of systems studied P was the limiting nutrient. In the mixoeuhaline sections of most systems N:P ratios were, however, lower, and indeed N limitation was evident in salinities above 30 in five of the estuaries studied. A decrease in the input of a limiting nutrient may reduce overall estuarine primary production. This can cause a negative feedback response whereby no change or indeed an increase in nutrient concentrations occurs. For example, in the Bandon Estuary, where P is the limiting nutrient, chlorophyll concentrations decreased in concurrence with riverine P inputs while MRP and DIN concentrations in the estuary both evidenced an increase. The significant decrease in pelagic primary production in the estuary would result in a consequential decrease in N and P assimilation. This could explain the increase in nutrients observed.

The direct effect of reducing P inputs on the phytoplankton biomass in the Bandon Estuary reinforces the findings of O'Boyle *et al.* (2015). This work described the importance of modulating factors in the responses of estuarine primary producers to nutrient conditions. Some systems, such as the Bandon Estuary, have high nutrients coupled with high phytoplankton biomass as they are not restricted by light or residence time. They will also respond very strongly to either an increase or a reduction in nutrient inputs. This in turn will impact on the uptake, cycling and retention of nutrients in the system. Similarly the Blackwater Estuary, also considered to be less limited by mitigating factors, exhibits a significant reduction in chlorophyll with a corresponding reduction in N and P inputs. Estuarine P concentrations do respond to the reduction in P inputs while a lack of reduction in estuarine N concentrations may be due to the decrease in biological uptake rates (Ní Longphuirt *et al.*, 2015a).

Nutrients received from the catchment system are filtered through both benthic and pelagic primary production within an estuarine system. A shift in the relative biomass of primary producers and the subsequent alterations to burial and regeneration of organic matter will reduce the amount of a nutrient that is retained within a system and, likewise, exported to the coastal zone (Paerl *et al.*, 2004). Furthermore, reductions in primary production can reduce denitrification rates as the carbon supply to the benthic system can decrease (Fulweiler *et al.*, 2007).

The impact of moderating factors could also explain the lack of biological response of some estuarine systems to decreasing inputs and estuarine concentrations. Physical factors such as residence time, ocean exchange and light availability can have a more important role in controlling primary production than high nutrient concentrations in these systems. Thus, even when concentrations and inputs have decreased the impact on growth is limited (O'Boyle *et al.*, 2015). This may explain the historically low chlorophyll concentrations and lack of response to nutrient controls in a number of systems. For example, the Liffey Estuary, Upper Blackwater, Maigue Estuary and Fergus Estuary are all limited by short residence times; the Lower Suir, Lower Corrib and Erne Estuaries have high ocean exchange rates; while the Shannon Estuary is limited by light availability.

Seven estuarine sections have been shown to be predominantly influenced by nutrients, with residence time and light conditions being considered secondary controls (O'Boyle *et al.*, 2015). Four

of these (Lower Bandon, Lower Blackwater, Moy and the Deel Estuary) showed a biological response to reductions in nutrient inputs. The remaining three systems classed as being primarily influenced by nutrients (Upper Bandon, Lower Slaney and Upper Suir) all evidenced high chlorophyll concentrations as a result of persistently high nutrient concentrations. These systems, while still showing signs of nutrient-related problems, can be predicted to respond well to tighter nutrient load controls.

In the Suir and Slaney systems reductions in P riverine inputs are not mirrored in the estuarine system and may relate to complex nutrient cycling that occurs in estuarine sediments. The accumulation of internal nutrient pools and their subsequent release from estuarine sediments can maintain nutrient concentrations at high levels in estuarine systems even when loadings have been reduced (Boynton *et al.*, 1995; Conley *et al.*, 2000; Carstensen *et al.*, 2006). This can compound the response of nutrient concentrations and, indeed, primary production to nutrient input reductions, especially where suspended sediments are high (Balls *et al.*, 1997). In these systems MRP–salinity curves indicate a bell shape with increases in MRP between 10 and 20 salinity confirming the importance of these nutrient pools (Fig. 9).

The importance of nutrient cycling in estuarine sediments is also an important factor in moderating the response of the system to seasonal changes in nutrient loads. In the Blackwater system, for example, trends in riverine nutrient inputs mainly occurred in winter and suggested the influence of closed spreading periods (Ní Longphuirt *et al.*, 2015a). Interestingly, this winter reduction appeared to have implications for summer biological responses. The results would suggest that sequestration of nutrients in benthic and intertidal sediments during winter periods, and indeed between years, may have implications even in summer when inputs may appear to remain stable Internal sediment pools of N can take up to 10 years to reduce (Christensen *et al.*, 1994) and, as such, could alter the importance of N fluxes from the sediment to the water column.

Finally, the influence of downstream point sources and adjacent systems on estuarine nutrient concentrations was shown to be an important factor in a number of estuaries. An example of this is the Garavogue Catchment. Riverine inputs to the Garavogue Estuary show a reduction in P but not N. However, inconsistently, no reductions in either nutrient were noted in the mesohaline section. The polyeuhaline and mixoeuhaline areas show significant reductions in N and chlorophyll; these reductions can be linked to decreases in the point source inputs due to improvements in the Sligo WWTP discharging to the estuary. A similar situation can be observed in the Moy, whereby reductions in estuarine concentrations are not preceded by reductions in riverine inputs. Such improvements, particularly in relation to P, are undoubtedly related to the upgrading of the WWTP in Ballina *c.*2008.

The Liffey and Tolka Estuaries, with catchments that contain the agglomeration of Dublin, have both evidenced negative changes. The Liffey Estuary shows increases in DIN that salinity–DIN plots suggest are linked to the impact of the Ringsend WWTP at the mouth of the estuary (Fig. 10). Concurrently the Tolka Estuary has exhibited an increase in chlorophyll since 2000 and very little change in the large opportunistic macroalgal blooms that occur in summer (R. Wilkes, 2016, personal communication). This is contrary to the large decrease in riverine inputs of both P and N. The Tolka Estuary is largely controlled by exchange with the adjacent Liffey Estuary and Dublin Bay, and hence the undesirable biological response of the primary producers is more than likely related to its proximity to the WWTP outlet combined with the provision of P from the outer Dublin Bay. The importance of marine sources of P for a similar marine-dominated system has been described in detail in Ní Longphuirt *et al.* (2015b).

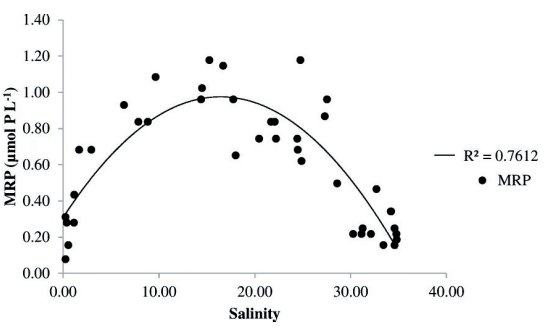


Fig. 9—MRP-salinity curve for the Suir Estuary from 2 July 2013, illustrating the bell-shaped relationship between these two parameters in this system.

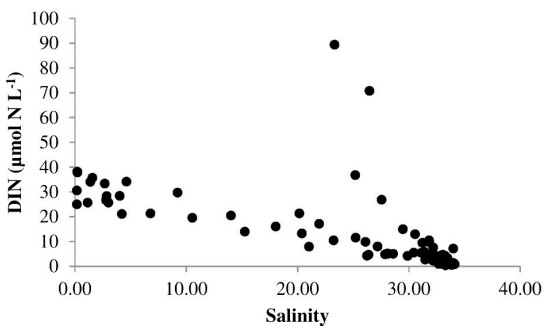


Fig. 10—DIN-salinity curve for the Liffey Estuary representing all data points in 2010. The divergence from the straight line relationship between DIN and salinity is indicative of the influence of the Ringsend WWTP facility at the lower end of the estuary.

Shifting baselines relating to climatic change or large-scale hydro-morphological changes mean that recovery of systems to pre-disturbance ecosystem status may in some cases be unreachable (Duarte *et al.*, 2009; Carstensen *et al.*, 2011). While not considered in this study, such changes will certainly be a factor in the response mechanism of Irish systems and deserve additional attention.

INFLUENCE OF LOAD SOURCE IN DETERMINING THE NUTRIENT LANDSCAPE OF ESTUARINE SYSTEMS

The results highlight the importance of nutrient load source in determining the nutrient landscape of estuarine systems. High DIN concentrations in the mesohaline and polyhaline sections of some systems (Bandon, Lee, Blackwater, Suir/Nore/Barrow system, Slaney and Boyne) are coupled with low MRP concentrations and result in relatively high N:P ratios. These catchments are receiving over 90% of their total N load from agricultural sources. This link is more important in the context of the increase in the N:P load ratio from agriculture since 2000 (Table 2). With the exception of the upper Slaney, these systems are also all classified as of 'Moderate' or 'Poor' status under the WFD. The classification is the result of diminished biological status rather than nutrient considerations as P in these systems is below the Good/Moderate WFD boundary. N on the other hand is not considered for status below a salinity of 30 and so the status is reliant solely on the response of the biological and related biochemical (DO, BOD) elements. Interestingly, if DIN were included it would not alter the status of these estuaries as the biological response is sufficient to result in a decrease in status. The Slaney is the exception to this as the upper estuarine system does not evidence a biological response. This is probably due to the very low residence time (0.63 days) in this system, which allows nutrients to pass through without sufficient time for phytoplankton growth to occur.

High and increasing N:P ratios have led to the exacerbation of outer coastal eutrophication problems in a number of European systems (Paerl *et al.*, 2004; Kronvang *et al.*, 2005; van Beusekom, 2005). A recent study in the North Sea has evidenced a link between large N:P imbalances and major consequences for the growth, species composition and nutritional quality of marine phytoplankton (Burson *et al.*, 2016). As in the Irish context, this has been linked to the disconnect between N and P fertiliser application rate reductions (Glibert *et al.*, 2014) and the more effective removal of P in domestic and industrial wastewater (Grizzetti *et al.*, 2012). The latter is also evident in Ireland; however, the ratio increase in point sources is much smaller than that for agriculture (Table 2).

Effective control of eutrophication therefore requires a consideration of not just loads of N and P individually but also their relative amounts to ensure effective reduction of nutrients transported to both estuarine and subsequent coastal zones. While mitigation strategies often serve a dual function through the targeted reduction of one nutrient resulting in a concurrent reduction of another, focus on mitigating individual pathways by identifying critical source areas for N and P can help to target individual reductions where necessary (Melland *et al.*, 2014).

A number of downstream mixoeuhaline systems can be considered N limited, particularly in summer (Liffey, Tolka, Boyne), while in some systems N:P ratios are decreasing due to nutrient controls (Garavogue, Moy, Corrib, Erne, Shannon). The shift from P to N limitation along the freshwater–marine continuum is widely accepted (Howarth and Marino, 2006). However, the implications for management measures in the estuary and upstream catchment are important in the control of eutrophication through the entire system (Paerl *et al.*, 2014).

CONCLUSIONS

Studies that trace N and P flows from source to the coastal zone allow not only determination of the effectiveness of mitigation but also enhanced understanding of response trajectories. This will assist in the future targeting of actions to be applied specifically in light of current and future programmes of measures. In most Irish systems studied, the greatest overall contributor to N and P loads is diffuse sources. However, reductions in both diffuse and point sources have resulted in considerable reductions in P, highlighting the effectiveness of measures that have been applied. Reductions in N loads have been more modest and are largely related to improvements in agricultural management. The high and increasing N:P ratios in river inputs and estuarine concentrations are an indication of the imbalance in nutrient reduction, which may have deleterious impacts for the transport of nutrients to the outer coastal zone. In the Irish context, this study has shown that the impact of measures to reduce nutrient loadings is largely dependent on not only load source but also nutrient cycling processes and modulating factors such as light and residence time. The influence of measures, cycling and physical controls will evolve through the estuarine continuum from fresh to marine water, highlighting the need to consider the impact of measures on each river–estuarine system in the context of these control shifts.

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