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ABSTRACT

The River Liffey is the main source of diffuse nutrients to Dublin bay and accounts for some 85% of all riverine inputs. The total load from the various rivers has been calculated at some 6601 kg $N.d^{-1}$ and 748 kg P. d^{-1} , of which around 82% and 52% are in the form of DIN and phosphate respectively. Sewage discharge adds almost the same again to the load, with minor contributions from the sediments (which may simply be remineralising the particulates) and from nitrogen fixation. However, these inputs are very much less than those exchanged twice-daily by tidal action. These contributions are due to change very shortly with the advent of the new STW in Dublin, but the major change may be more in the speciation of the nutrients, and in particular the dissolved/particulate balance.

Keywords: diffuse inputs, nutrients, Dublin Bay

INTRODUCTION

Dublin Bay has som eproblems with eutrophication, in the form of excess macroalgal growths, suggesting some dysfunction in the system as a whole (ERU 1992; Brennan *et al.* 1994). Surveys of the benthic fauna (Walker & Rees 1978, Wilson 1982), of long-term changes in some components (Wilson 1997) analysis of benthic community structure (Roth & Wilson 1998) and a preliminary network analysis of intertidal and subtidal combined (Wilson & Parkes, 1999) point to a range of problems in the way that the system functions, and these indications are reinforced by pollution indices indicating considerable local problems (Jeffrey *et al.* 1985, 1991, Wilson & Jeffrey 1994).

Significant levels of persistent contaminants such as heavy metals are largely confined to the upper parts of the Liffey and Tolka estuaries, and to a lesser extent that of the Dodder. Jones & Jordan (1977) reported a gradient of metal contamination from the entry of the Camac to the harbour mouth. Subsequent surveys (Wilson *et al.* 1986, Brennan 1988, Britton 2001) have shown to an overall decline in metal levels with the closure of certain industries and the upgrading of the Victorian sewage system. In the Tolka estuary, levels show some signs of a decline since Jeffrey *et al.* (1978), but the indications are by no means so clear-cut, and have been complicated by considerable works and reclamation in the innermost (and previously most contaminated) sections (Wilson 2003). Contaminant levels in the Dodder are low compared to those in the upper Liffey (O'Brien 1997). Data on other categories of persistent contaminants are scarce, but suggest that the levels, while measurable, are not particularly elevated in comparison to similar situations elsewhere. Concentrations of hydrocarbons and PAH's were, like the metals, highest in the inner parts of the harbour and Tolka estuary, but were elsewhere not notably elevated even in the muddy lagoons (Choiseul *et al.* 1995). Imposex induced in gastropods on exposure to TBT and other organotins has been detected all over Dublin Bay (Shaw 1998, Cox 2001), even well out into the deeper water where no other traces of contamination have been detected (Dempsey 2000).

There has been considerable work done on nutrient inputs to the Bay, with many studies emphasising the role of particulate nutrients in the system and their contribution to algal growth though remineralisation (Jeffrey *et al.* 1991, 1995, Jennings 1996, Khan 1998). These particulate nutrients, along with dissolved forms, are brought into the system by both sewage discharge and the rivers to mix in the Bay with inputs and outputs through tidal exchange. This paper examines the diffuse (*i.e.* non-STW) inputs of nutrients into Dublin Bay and the influence of driving forces such as run-off.

MATERIALS AND METHODS

The river and canal inputs into Dublin Bay are listed in Table 1. Details of the analyses for the various nutrient species are set out in detail in Brennan *et al.* (1994), but may be summarised as follows:

Dissolved nutrients were defined as those passing through 0.45 μ m filters, with particulate nutrients retained. Ammonium was determined with a Tecator dye (5000-0295), while NO_X included both nitrate and nitrite and was determined spectrophotometrically, following cadmium reduction/sulphanilamide reaction. The detection limit for both was 10 ug Γ^1 . Dissolved inorganic nitrogen (DIN) = ammonium + NO_X, and total nitrogen (TN) = KN + NO_X, while dissolved organic

nitrogen (DON) + particulate nitrogen = TN - DIN. Dissolved inorganic phosphate (DIP or $PO_4^{3^-}$) was measured by the ascorbic acid reduction method of Murphy and Riley (1962) and the detection limit was 1 ug I¹. Dissolved organic phosphorus (DOP) + particulate phosphorus (ptc P) = TP - DIP. A 25 ml sub-sample was digested by the Kjeldahl method (modified after Rand *et al.*, 1992) to determine kjeldahl nitrogen (KN) and total phosphorus (TP). Organic carbon (POC) and total nitrogen (ptc N) in the particulate component on the filter was determined on a LECO CNS-1000 analyzer. The limit of detection was 0.02 mg g⁻¹ for C and 0.02 mg g⁻¹ for N.

Table 1. Mean annual FW inputs (10 ³	n ³ .d⁻¹	¹) and concentrations (mg.l- ¹) of suspended solids (SS), total nitrogen
(TN) and total phosphorus (TI	P). Da	ta from Crisp (1976), ERU (1992) and Brennan <i>et al.</i> (1994).

<u>Input</u>	Flow	SS	TN	TP
R. Liffey	1641	12.25	2.80	0.32
R. Dodder	207	10.56	2.33	0.23
R. Tolka	147	14.10	3.88	0.34
R. Camac	96	9.55	3.97	0.39
R. Poddle	48	4.34	2.93	0.31
Royal Canal	32	4.22	1.38	0.15
Grand Canal	32	2.64	2.33	0.13
R. Santry	15	4.91	5.52	0.38
R. Nanniken	2.6	3.79	5.22	0.44

RESULTS

Riverine input of nutrients into the Bay was dominated by the River Liffey (Fig. 1, Table 1). Of the small streams and drains, the Santry and the Nanniken were the only ones to carry any appreciable amount, and then only under storm conditions, when flows approached 1.0 m³.s⁻¹. There was relatively little difference between the inputs in terms of SS or nutrient concentrations, with N and P concentrations in the Tolka being slightly higher than those from the Liffey, with those from the Dodder being rather lower still (Table 1). In the two canals total P was markedly lower than from any other source.

A similar pattern was seen more or less across all contributions of the different nutrient species to the totals (Table 2). For N, DIN contributed the highest proportion, with NO_X in turn being the major component, with lesser contributions from particulate and dissolved organic N (DON). P inputs however, were much more balanced between particulate and dissolved phases, although again the canals stood out, with the P input from the Royal Canal being almost all particulate (Table 2). Molar C:N:P ratios for particulate inputs were around the Redfield ratio of 106:16:1, suggesting labile and rapidly mineralisable substrates.

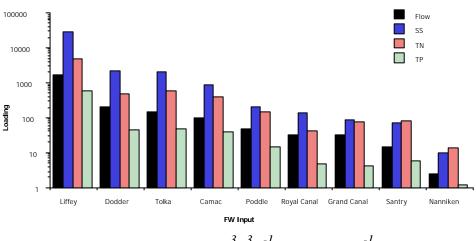


Fig. 1. Freshwater flow $(10^3 m^3 d^{-1})$ and input $(kg.d^{-1})$ to Dublin bay.

There was little evidence of a seasonal signal in the nutrient inputs, although any pattern was distorted by the opening of the sluices for the Liffey descent in June (Fig. 2). The flow recorded on the 15th June (JD 165) was just under $5.5*10^{6}$ m³.d⁻¹, over three times the long-term average (Table 1). Loads increased with flow, although it is worth noting that while SS increased exponentially with flow (best-fit, $r^2 = 0.91$), N and P loads increased linearly (best fit, $r^2 = 0.94$ and $r^2 = 0.84$ respectively). These relationships held whether or not the exceptional flows of JD 165 and 166 were included in the data set. The speciation of the inputs changed with flow, with logarithmic decreases in the DIN/TN and DIP/TP ratios with increased flow. These relationships for dissolved species, although still significant ($r^2 = 0.48$ and 0.29, p< 0.01 and <0.05 for DIN/TN and DIP/TP respectively), were not as strong as those for total nutrients, suggesting that there was a mix of mechanisms involved.

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Table 2. Nutrient speciation (mean % contribution to total load) in inputs (- indicates PON and DON not
distinguished).

Input	DIN	NO ₃ -	P+DON	PON	DON	SRP	P+DOP
Liffey	70.5	66.6	29.5	10.3	19.2	24.7	75.3
Dodder	82.0	79.7	17.9	13.5	4.4	25.7	74.3
Tolka	87.7	85.5	12.5	9.1	3.2	46.2	53.8
Camac	82.4	79.5	17.6	-	-	48.0	52.0
Poddle	88.6	87.6	11.4	-	-	35.1	64.9
Royal	51.1	42.3	48.9	-	-	1.9	98.1
Grand	81.9	79.9	18.2	-	-	2.5	97.5
Santry	89.4	88.5	10.6	-	-	38.7	61.3
Naniken	86.8	84.6	13.2	-	-	51.1	48.5

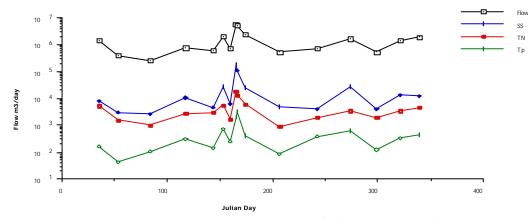


Fig. 2. Seasonal pattern of discharge $(m^3.d^{-1})$ and load $(kg.d^{-1})$.

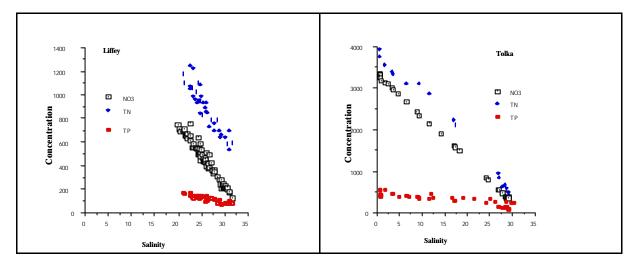


Fig. 3. Nitrate (NO₃), total nitrogen (TN) and total P concentrations (ug.l⁻¹) with salinity in Liffey and Tolka estuaries.

Tidal cycle data from both the Liffey and the Tolka (Fig. 3) suggest that the major nutrient loads are associated with the freshwater inputs. While the two cycles in the Liffey were virtually the same, those for NO_X and TN in the Tolka were quite distinct (in Fig. 3 only one set is shown for clarity) and their regressions have been calculated separately (Table 3). There were strongly significant relationships for both N and P in all their forms, with the exception of NH₄ (Table 3). SS in the Tolka appeared to be of marine origin (Table 3).

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Table 3. Nutrient concentrations and SS (y) with salinity (x) in the Liffey and Tolka estuaries showing linear regressions y = mx + c, correlation cofficients (r²) and significance (* p<0.05, ** p<0.01). See also Fig. 3 and text.

	Parameter	m	с	r ²
Liffey				
	NO3	-53.24	1817	0.96**
	NH4	7.67	-115	0.14
	TN	-60.85	2456	0.86**
	DIP	-4.38	172	0.67**
	TP	-8.63	346	0.77**
	SS	0.188	7.94	0.05
Tolka				
	NO ₃	-103.6	3358	0.999**
	NO ₃ (2)	-63.7	2124	0.99**
	NH4	1.75	98.7	0.08
	TN	-114.9	3943	0.99**
	TN(2)	-62.0	2360	0.96**
	DIP	-3.68	168	0.92**
	TP	-10.73	500	0.80**
	SS	0.50	5.91	0.62**

OTHER DIFFUSE INPUTS

Other diffuse inputs of nutrients into Dublin Bay include those from the sediments, from the biota, from atmospheric deposition, from groundwater and from nitrogen fixing.

Rates of N release from the sediments in Dublin Bay can be very high, with NH₄ fluxes of up to 27.15 mgN.m².h⁻¹ measured from core incubations (Brennan *et al.* 1994). However, this was an exceptional reading from a polluted mud in summer in the Tolka estuary, and the rates for the rest of the sediments throughout the year are very much less. Average rates from Brennan et al. (1994) were 10.1 mgN.m².h⁻¹ for the Tolka estuary as a whole, 2.66 mgN. m².h⁻¹ for the South mgN. m⁻².h⁻¹ Lagoon, 0.57 mgN. m⁻².h⁻¹ for the North Lagoon and 0.25 mgN. m⁻².h⁻¹ for the remainder of the Bay, giving a total annual input from the sediments of some 230 tN.y⁻¹.

The fauna likewise are a source of N from NH₄ excretion from metabolism. Wilson & Parkes (1999) have calculated a detailed size-structured respiration (metabolism) budget for the Dublin Bay fauna (5197 kj.m⁻².y⁻¹), which can be converted to N excretion by using an average O:N ratio of 30. This yields a faunal NH₄⁺ input to Dublin bay of 309 tN y⁻¹. Atmospheric deposition of N in Dublin has been measured at 3.15 mgN. $m^2.d^{-1}$ (Bailey & Dowding 1987). As a conservative estimate, this is equivalent to 41.6 t.y⁻¹ over the open part of the Bay. There are a considerable number of groundwater flows under Dublin, but little is known of their outflow into the Bay. The DBWQMP (ERU 1992) estimated an annual input of 19 tN, and from concentration ratios around 1 tP into the Bay through groundwater. For N alone, nitrification may be also an input. Blue-green algae are largely unstudied in DB, although they have been recorded around Bull Island in both saltmarsh and lagoonal mudflat (Jeffrey 1977) Assuming average rates of around 2mg N. $m^2.d^{-1}$ (McGlathery *et al.* 1998) for N-fixing for the muddy habitats gives just 9.1kg N d⁻¹.

Much less data are available for P. Parsons & Wilson (1997) studied PO₄ release from *Hydrobia* and sediments in DB and found that they were around 5% of those for NH₄ Applying this figure to those above for sediments and fauna gives an estimate of 11.5 tP y⁻¹ and 15.5 tP y⁻¹ respectively. Atmospheric P deposition is likewise a small fraction of N input. Jassby *et al.* (1995) estimated atmospheric P input to Lake Tahoe at about 2.5% of that of N, equivalent to 1.04 t.y⁻¹ into Dublin bay.

Finally, there are inputs with every tidal exchange. Wilson & Parkes (1999) have calculated the tidal prism as 5.8×10^6 m³, which means that every tidal exchange brings in around 16704 kg N and 3944 kg P to Dublin Bay, of which 43% and 35% respectively are in the dissolved forms (Brennan *et al.* 1994).

DISCUSSION

The total input of nutrients from diffuse sources into Dublin Bay is 7202 kg N.d⁻¹ and 777 kg P.d⁻¹ (Table 4). Neither of these are very imposing totals put beside those of major rivers, for example the Mississippi, the Rhine or the Thames, which are larger by some orders of magnitude. This is largely a function of flow, as the levels of nutrients are similar to those reported here. For example Rabelais *et al.* (2002) report long-term mean nitrate concentrations in the Mississippi equivalent to 3.2 mg.l⁻¹ N which is close to the nitrate concentration in most of the riverine inputs to Dublin bay.

Source	Ν	P
Rivers	6601	748
Sediment remineralis ation	230	11.5
Faunal metabolism	309	15.5
Aerial deposition	42	1.0
Groundwater	19	1.0
Fixation	9	-
Non-marine Total	7202	777
Tidal prism loading	16704	3944

 Table 4. Summary of diffuse nutrient inputs (kg.d¹) to Dublin bay and tidal prism loading.

 Source
 N
 P

The riverine diffuse inputs into Dublin Bay are also rather slight against the tidal exchanges (Table 4), each of which brings in almost the same amount of nutrient in readily available dissolved form as the rivers bring in total in a day. To this also has to be added the sewage contribution, which delivers three times as much N and about the same amounts of P to the Bay as the rivers (Wilson *et al.* 2002). Data from the waters off Dublin show that the dissolved nutrient inputs are quickly absorbed into the surrounding Irish Sea and that the impacts of the Liffey plume are confined to the waters inside the Kish bank (ISSG 1991, Nixon *et al.* 1998). This rapid dilution is undoubtedly due to the hydrodynamic nature of the Bay, where tidal currents can reach up to 0.5 m.s^{-1} , and may be a factor in the relative infrequency of phytoplankton blooms off Dublin (McMahon & Silke 1998).

The particulate nutrients, however, are somewhat less easily exported. O'Dowley's particulate transport model (Brennan *et al.* 1994) suggested that the current movements round Dublin bay created an area of deposition just outside the port entrance. This area coincided with an unusually dense bed of *Lanice conchilega*, a tubicolous polychaete with which the macroalgae *Ectocarpus* in particular is associated and the assemblage forms one of Jeffrey's (Jeffrey *et al.* 1991, 1995) remineralisation foci.

The contribution of the sediments to nutrient input is minor in comparison to the overall riverine input, but this generalisation hides several important considerations. Firstly, there is spatial heterogeneity in sediment distribution, such that they constitute a source of N in the muddy areas, but an actual sink of N over much of the sands, since in these coarser sediments NO₃ uptake actually exceeded NH₄ release (Brennan *et al.* 1994). Thus the sediment contribution could probably be much reduced or even ignored completely in terms of the wider function of the Bay. However it remains crucial in the lagoons, where the remineralisation is implicated in the macrolgal blooms, although the recent evidence suggests that it is the sewage rather than riverine particulates which fuel the sediments (Jennings 1996). The other contributions likewise are minor and even N fixation or denitrification is unlikely to be of more than small-scale significance. The salinity/concentration relationships in Fig. 3 show practically classical conservative behaviour by the nutrients, suggesting little or no modification between riverine input (i.e. atmosphere or groundwater) were of importance only where the riverine input itself was limited, but they did demonstrate the importance of sediment burial in the overall nutrient budget. This is a mechanism which might be usefully investigated in Dublin bay, especially given the strong algae/sediment remineralisation linkage. Nutrient budgets calculated for the South Lagoon in Dublin bay have shown no marked import/export trend and the whole system may be more stochastically-driven than predicted (Wilson *et al.* 2002).

The origin and the role of diffuse inputs and the link with eutrophication has received increasing attention in recent years, but there is still some way to go in terms of our understanding (Wood, 1998). Vollenweider's P models and their derivatives have proved their worth in freshwater, but estuarine and marine models are still to be developed. While system models do exist (e.g. Soetart & Herman1995), they are relatively insensitive in terms of nutrient delivery and speciation, and this understanding is required if we are to successfully manage coastal and transitional waters.

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