

Periphyton - nutrient relationships in rivers

A literature review and New Zealand perspective

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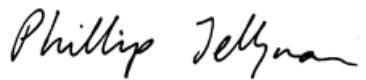
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Executive summary

Management of the direct effects of nutrient enrichment in rivers in New Zealand are addressed in the 2014 National Policy Statement for Freshwater Management (NPS-FM), through inclusion of an attribute for assessment of periphyton (benthic algae). Periphyton responds directly to nutrient changes (i.e., eutrophication) in rivers and periphyton abundance (standing crop) above certain thresholds can impair ecosystem health. Management of periphyton is particularly relevant to the dairy industry, because land use for dairying can lead to increased runoff and leaching of nutrients to waterways.

DairyNZ, the industry organisation that represents all New Zealand dairy farmers, requested a literature review of current knowledge about relationships between periphyton and nutrient supplies in rivers. The purpose of the review was to assist understanding of how management actions that potentially change nutrient inputs to waterways might affect periphyton standing crop. The review may be used as an information source for DairyNZ when queries arise about land use or management changes, or other aspects of dairying and associated activities that might potentially affect periphyton in rivers.

The review first summarises characteristics of rivers in New Zealand that may distinguish them from rivers in other parts of the world (in terms of the factors that influence periphyton). Distinguishing factors include: characteristic and variable flow regimes, high proportion of undeveloped low-order streams in some regions, limited seasonal effects on nutrients from deciduous leaf fall, low levels of nitrogen deposition.

The review focussed on **periphyton standing crop in the wadeable areas of cobble-bed Hill or Mountain rivers** (as defined in the River Environment Classification). Literature was included where periphyton was measured as **chlorophyll *a***, because chlorophyll *a* is used for the NPS-FM attribute. Reference to percentage cover and taxonomic composition is included in some cases. Periphyton **growth** or **growth rates** refer specifically to the rate at which algal cells grow and divide within periphyton. Throughout the review, “nutrients” refers to nitrogen (N) and phosphorus (P), mainly as **dissolved inorganic nitrogen (DIN)** and **dissolved reactive phosphorus (DRP)**.

Nutrient supplies play an important role in driving periphyton growth: as a general rule, increasing nutrients = higher algal growth rates. Caveats to this relationship include: (a) other factors such as light or micronutrients are not growth-limiting, and (b) nutrients can promote periphyton growth only up to the point where nutrient concentrations are saturating.

A theme of the review was that relationships between nutrients and periphyton **growth rates** are rarely mirrored by equally clear relationships between nutrient concentrations in overlying river water and periphyton **standing crop**. One reason is that periphyton standing crop (as distinct from growth rate) is influenced by other factors (such as invertebrate grazing and river hydraulics). Another important reason is that survey locations and sampling techniques can influence relationships. Standardising sampling to runs in rivers (rather than riffles or pools), ensuring sufficient sampling replication to account for spatial variability at a site, and conducting time-series studies to enable estimation of peak standing crop, should all help to reduce “noise” in the resulting patterns. Consequently, the periphyton attribute in the NPS-FM was developed with a requirement for time-series monitoring.

The review considered: variability in nutrient supplies to periphyton over space and time (including nutrient cycles and spiralling in rivers); an overview of typical nutrient concentrations in New Zealand

rivers including seasonality; relationships between periphyton standing crop and nutrient concentrations along rivers (longitudinal) and between rivers; effect of seasonal patterns in nutrient concentrations on periphyton standing crop, and vice versa; saturating concentrations of N and P; the effects of non-nutrient factors on relationships between periphyton standing crop and nutrient concentrations; alternative sources of nutrients and legacy sources; and effects of river size.

Spiralling of N and P in rivers involves transformations from bioavailable to unavailable (organic) forms and subsequent recycling. DIN and DRP are removed from streams through biological uptake (by periphyton), by denitrification (for N, direct conversion to nitrogen gas) and by adsorption or binding to metals and particles (for P). At the scale of a river reach, removal processes are influenced by nutrient concentration and temperature; biological removal and recycling are affected by water velocity, light, temperature, and biological capacity (type and amount of algae). Few studies were located in which nutrient removal was compared with periphyton standing crop.

Seasonal fluctuations of nutrient concentrations in many rivers are driven by a combination of hydrology and biological uptake. Based on patterns seen at the 77 sites in the National River Water Quality Network (NRWQN), most New Zealand rivers show annual maxima in DIN in winter and minima in mid-summer. Fewer rivers showed seasonal patterns in DRP. The seasonal patterns in DIN are likely to be at least partly driven by seasonal flow patterns, but other processes (including catchment and instream uptake) must drive seasonality at some sites. Nitrogen-fixing vegetation and stock-related discharge in the catchment may contribute to seasonal N-leaching.

Studies were reviewed of periphyton standing crop (generally measured as chlorophyll *a*) in relation to N and P at multiple sites along the same river, and in surveys at sites in different rivers and catchments in the same region. In **longitudinal studies**, periphyton chlorophyll *a* gradients along rivers generally corresponded to N and P gradients, although gradients in other environmental factors (such as substrate size) were also linked to chlorophyll *a*. Therefore, the absolute values of chlorophyll *a* linked to different N and P concentrations varied across rivers.

In the review of **between-river studies**, most synoptic surveys of multiple sites in different rivers and catchments did not show strong relationships between periphyton standing crop (as chlorophyll *a*) and nutrient concentrations, but there were exceptions. In some cases, a lack of relationships between periphyton and nutrient concentrations could be explained by other environmental differences between the sites. A between-river study in New Zealand that showed relatively strong periphyton – nutrient relationships used time-averaged mean nutrient concentrations and maximum chlorophyll *a*, and included a term to account for accrual period.

Little information was located on the effects of **seasonal changes in nutrient concentrations** on chlorophyll *a*, probably because these seasonal changes coincide with flow changes, which have an overriding effect on periphyton. The potential effect of periphyton on removal of nutrients from the water column was evaluated. The conclusion was that nutrient removal is generally negligible except in long periods of declining water depth over long, shallow, stream reaches, when starting concentrations are low.

Few studies examined chlorophyll *a* versus nutrient concentrations over time. The best example was a study at multiple sites on a single river over 12 years. Management-led reduction of P resulted in chlorophyll *a* reductions at sites where P fell below concentrations thought to saturate growth.

Saturating concentrations of DIN and DRP (i.e., above which periphyton standing crop no longer increases) were suggested in some studies. Estimates for DIN were 230 – 280 mg m⁻³. The

corresponding values for DRP appears to be $\sim 28 \text{ mg m}^{-3}$. Note that these concentrations were derived as average values statistically linked to a flattening of the positive relationship between concentration and standing crop. It is possible that they would be biased towards low values if the dataset contains sites where other factors (such as micronutrients or light) limit standing crop. Maximum chlorophyll *a* corresponding to the suggested saturating concentrations was variable, ranging from ~ 100 to $\sim 350 \text{ mg m}^{-2}$. The chlorophyll *a* threshold defining the bottom line in the NPS-FM (200 mg m^{-2}) was exceeded at DIN from 170 to 4000 mg m^{-3} and DRP from 5.7 to $> 70 \text{ mg m}^{-3}$, indicating great variability across rivers.

Factors that have **interactive effects on periphyton – nutrient relationships** include river flows, geomorphology (at the reach scale and rock scale), shading, invertebrate grazing and water chemistry. The effects of river flows, and in particular flood frequency, on periphyton are well understood, have been the topic of considerable research in New Zealand. Comprehensive reviews are available elsewhere; therefore periphyton – flow interactions are covered only briefly in the present review. For the remaining interactive factors, examples are presented of conditions under which each may modify how periphyton standing crop responds to nutrient enrichment. An idealised model is presented for assessment of sites that may represent “hot spots” for high periphyton standing crop.

Supplies of nutrients to periphyton largely originate in the water column. However, sediment can be a significant source of P to periphyton. P from this source can represent a long-term **legacy from past land-use practices**, maintaining high standing crop despite low DRP concentrations in the water column. Legacy-sourced DIN (generally from groundwater), or, in one example, increased DIN as an unexpected outcome of catchment management may also delay positive effects of current nutrient management.

Finally, the impact was considered of **river size** on nutrient removal (i.e., assimilation) and export from a stream reach. A conceptual model is presented, which shows that maximum benefit (i.e., lower periphyton biomass, while minimising DIN export to downstream reaches) is most likely if invertebrate grazing can be promoted in unshaded small rivers with moderate DIN concentrations.

This evaluation in effect identifies further “hot spots” in rivers that could be targeted and managed for maximum removal of nutrients from the water column, specifically small, unshaded streams with good habitat for invertebrates (i.e., fast-flowing riffles). For DIN, mitigation may be ineffective in both small and large rivers where DIN concentrations are already high (e.g., $> 1000 \text{ mg m}^{-3}$). In that case, taking direct steps to reduce DIN inputs to the waterway may be the only option for mitigating high periphyton chlorophyll *a* and avoiding export downstream. Research in New Zealand is needed to establish thresholds of DIN below which mitigation is possible.

Generalisation of steps to reduce DRP availability to periphyton in streams is more complex than for DIN. A high proportion of P is delivered to streams in particulate form (bound to sediment), from which algae can access P directly under certain conditions. A further complication is that sediment-bound P is more readily trapped within reservoirs, lakes and floodplains than N. Nevertheless, uptake of DRP, like DIN, is most rapid in small, shallow streams. Periphyton can also utilise P from sediment sources in these environments and the mechanisms for accessing P vary according to water chemistry and river geomorphology.

1 Introduction

Rivers worldwide are increasingly under threat of ecological damage as a result of water abstraction and diversion, direct point-source pollution, and increased nutrient runoff following catchment land-use changes (Foley et al. 2015). Ecological damage can be defined as disruption to the natural food-web of rivers, and may affect all trophic levels both directly and indirectly.

An important component of ecological damage to rivers affects the base of the food chain – primary production, primarily benthic algae or periphyton (Stevenson et al. 2102). Periphyton is a natural component of river and stream ecosystems, providing food for many aquatic invertebrates which, in turn, are food for fish. However, in suitable conditions, periphyton can proliferate to high levels. Favourable conditions for proliferations include: low, stable flows and water velocities, stable substrates, nutrient enrichment (especially nitrogen, N, and phosphorus, P), high sunlight and warm water temperatures (Biggs 2000b). High levels of periphyton have the potential to change dissolved oxygen concentrations and pH to levels that are stressful to invertebrates and fish, and to adversely affect recreational values (such as swimming and fishing) and reduce aesthetic values. Some types of periphyton have toxic effects on animals and humans (in the case of benthic cyanobacteria), clog water intakes, or make water unpalatable for stock drinking purposes.

In some parts of New Zealand, a visible land-use change over the past two decades has been the conversion of land previously used primarily for dry-stock farming or cropping to dairy pasture (Wilcock et al. 2013). Increased concentrations of bioavailable N and P in streams and rivers have been attributed to this change (Hamill & McBride 2007, McDowell et al. 2011, Ballantine & Davies-Colley 2014, Larned et al. 2016).

Management of the potential effects of all catchment activities on freshwaters was recently addressed at a national level in the National Policy Statement for Freshwater Management (NPS-FM) issued in July 2014 (NZ Government 2014). At this stage, the NPS-FM does not specify targets or thresholds for loads or concentrations of N and P to protect against the non-toxic, negative effects of nutrients because of large uncertainties in relationships between primary production (as periphyton) and nutrient concentrations when averaged across multiple rivers (Snelder et al. 2013). Instead, periphyton standing crop (determined as chlorophyll *a* per square metre of wadeable river bed) was included as an attribute in the NPS-FM for the direct assessment of negative effects of eutrophication on ecosystem health.

While implementation of the NPS-FM¹ is primarily the responsibility of regional councils, successful mitigation of any identified adverse effects on periphyton will ultimately be the result of catchment and land management with implications for dairy farmers. Providing tools, resources and advice to help dairy farmers improve their management of diffuse discharges is one of the remits of DairyNZ, the industry organisation that represents all New Zealand dairy farmers. DairyNZ's stated purpose is "to secure and enhance the profitability, sustainability and competitiveness of New Zealand dairy farming". One of the targets for achieving sustainability is "to minimise and mitigate any potentially detrimental effects on rivers and streams arising from dairying activities in their catchments" (<http://www.dairynz.co.nz/>).

In light of the requirements of the NPS-FM, DairyNZ requested from NIWA a literature review of current knowledge about relationships between periphyton and nutrient supplies in rivers. The

¹ Subsequently in this report, unless otherwise stated, the abbreviation NPS-FM is used to refer to the rules around the periphyton attribute in the National Objective Framework in the National Policy Statement for Freshwater Management (NZ Government 2014).

review was to include interactions with other environmental factors, and prospects for predicting responses by periphyton to changes in nutrient concentrations. The purpose of the review was to assist in understanding of how management actions to change nutrient inputs to waterways might affect periphyton standing crop. It is expected that the review will be used as an information source for DairyNZ when queries arise about (for example) land use changes or management changes, or other aspects of dairying and associated activities that might potentially affect periphyton. The brief was to include the effects of season, hydrological and hydraulic conditions, shading, temperature, stream size and sediment inputs, as well as direct relationships between periphyton and nutrients. Background information on nutrient cycling in streams was also requested.

River management under the NPS-FM assumes that ecological condition is reflected by periphyton standing crop measured as chlorophyll *a*. Chlorophyll *a* is a useful measure of periphyton abundance because all algal taxa contain this green pigment. However, periphyton always comprises multiple taxa. Chlorophyll *a* content may differ between taxa and taxa tend to have characteristic responses to environmental factors, including nutrients. Therefore, variability in standing crop is expected to be accompanied by variability in community composition. Periphyton community composition is referred to where it may have implications for periphyton (chlorophyll *a*) – nutrient relationships.

The review starts with an overview of the characteristics of rivers in New Zealand. Features of many rivers in New Zealand set them apart from those in, for example, continental USA or Europe. While small-scale within-stream processes may be applicable globally, generalisations of larger scale patterns such as seasonality and catchment interconnectedness based on data from elsewhere are not necessarily applicable to New Zealand.

A brief account follows of some contrasting approaches to the use of periphyton as a tool for river management. Management aimed at mitigating the ecological impacts of anthropogenically-sourced nutrient inputs on waterways varies across the globe. Variations arise as a result of considering different measures (or metrics) of both periphyton and nutrients, different spatial and temporal scales for application of regulations and standards, and different methods for assessing the efficacy of regulations.

A short “primer” on periphyton is then provided, leading into the main part of the review. This section summarises current understanding of the main drivers of periphyton standing crop, and explains the importance of accurate and consistent measurements of periphyton as the foundation for understanding relationships between periphyton and environmental variables, including nutrients. The remainder of the review, following the discussion of the New Zealand context, is divided into sections that consider:

- variability in nutrient supplies to periphyton over space and time (i.e., N and P cycling, differences along river continua, over different seasons, and under different flow conditions), of the year;
- patterns in dissolved inorganic N and P concentrations and periphyton cover in New Zealand, based on data from the National River Water Quality monitoring Network (NRWQN, Davies-Colley et al. 2011);
- a review of research into relationships between periphyton standing crop and nutrient concentrations along river continua, across river sites, and over time, including a discussion of the potential for instream periphyton to affect nutrient concentrations at certain times;

- interactions between N and P and other factors influencing periphyton abundance and community composition, such as hydrology / and river geomorphology, light (shading), invertebrate grazing and water chemistry (conductivity, major ions, and micronutrients).
- the potential for nutrient supplies (especially P) from sources other than the water column and from legacy effects to affect periphyton.

In a final section the prospects for prediction of periphyton responses to changes in nutrient supply are summarised. The feasibility of mitigation of unacceptable levels of periphyton in rivers is assessed, referring to interactions between nutrients and other factors in controlling periphyton standing crop.

2 Characteristics of New Zealand rivers

Much of the literature on river nutrients and linkages to periphyton is based on research in other regions. The relevance of overseas research to New Zealand needs to be considered, because rivers in New Zealand may be hydrologically distinctive in a global context. In a global comparison of river hydrological regimes, New Zealand rivers were found to be hydrologically most similar to rivers in Europe, but rivers in the two regions still formed discrete groups (Poff et al. 2006). Compared to rivers in all other regions, those in New Zealand have, on average, high variability in negative changes in flow, high baseflow indices, high minimum flows and high flows in the spring months compared to rivers in other regions (Poff et al. 2006).

The ecological consequences of hydrological variability in New Zealand Rivers have been summarised in terms of a hierarchy of temporal scales, with variability over periods of months being the most relevant to instream biota including periphyton (Biggs et al. 2005). Month-to-month variability includes seasonality, and Biggs et al. (2005) proposed that waterways fell into three major classes of seasonality:

1. Mountain rivers, in which high flows are most common in spring as a result of snow melt combined with rain-bearing westerly airflows. A few rivers are also glacier-affected, which leads to generally low flows in winter and highest from through spring and summer (Owens & Fitzharris 2004);
2. Hill rivers, especially in the east of the country, in which lowest flows occur during summer to autumn and highest flows in winter;
3. Spring-fed streams, which are predominately groundwater-fed waterways that have more or less constant flows year round, although summer flows can be lower.

The main focus in this review will be on Mountain and Hill rivers, which generally have cobble beds with primary production dominated by periphyton. In contrast, spring-fed streams are characterised by macrophyte-dominated primary production rather than periphyton (Riis & Biggs 2001).

There is considerable variability within the Mountain and Hill categories, resulting from regional variability in climate, which leads to variation in patterns of seasonality (Duncan & Woods 2004). Within single waterways, year-to-year fluctuations in flow are generally not strongly predictable (e.g., McKerchar & Pearson 1994), especially when compared with many North American rivers in which seasonal patterns are primarily driven by snowmelt (Woo et al. 2008).

Early studies on periphyton in New Zealand demonstrated that temporal variation in periphyton standing crop within waterways is primarily determined by flow variability (in particular, flood frequency), through removal processes during high flows and ability to accrue during flood-free periods (Biggs 1995). The effects of nutrients on periphyton are superimposed on the effects of flow variability, so that nutrient supplies tend to be strong determinants of peak standing crop over an annual cycle (Biggs 2000a). Flow variability also influences the timing and supplies of nutrients to waterways.

Over 50% of New Zealand's total river length is drained by catchments with little or no significant development. Undeveloped upper reaches characterise Mountain rivers in general. The headwaters of Hill rivers can also be relatively unimpacted in some regions (e.g., parts of Canterbury, Otago and Southland), but more developed in others (e.g., North Island regions including Northland and Waikato). Published analyses of effects of headwaters on downstream nutrients (e.g., Alexander et

al. 2007) highlight that there is potential for catchment development in these headwaters to influence the stream ecosystem far downstream.

New Zealand streams and rivers differ from many waterways in temperate regions in the Northern Hemisphere in that, under natural conditions, riparian trees are evergreen. Therefore the streams are not subject to predictable autumn leaf fall, which introduces seasonal carbon and nutrients to river systems in regions where the tree flora is dominated by deciduous species (Mulholland 2004, Goodale et al. 2009). However, the middle and lower reaches of many Hill rivers, and some Mountain rivers, are now lined by introduced willows (Lester et al. 1994), which may have implications for stream ecosystems (McInerney et al. 2010a,b) as well as for nutrient cycling (Zukowski & Gawne 2006).

It is also worth noting that New Zealand has no native herbivorous fish. Periphyton can be a significant food source for freshwater fish in some regions (Jardine et al. 2012).

In terms of their chemical composition, New Zealand rivers are distinguished from those in the Northern Hemisphere by the relatively limited influence of atmospheric nitrogen deposition in the Southern Hemisphere (Lepori & Keck 2012). Concentrations of nitrate-N (as NO_3^-) and ammonium-N (as NH_4^+) in rainfall over New Zealand are generally much lower than in other parts of the world (Verhoeven et al. 1987, Vazquez et al. 2003, Liu et al. 2005, Willey et al. 2006), although this may be changing (Parfitt et al. 2006).

Within New Zealand, the different geological setting of the North and South Islands also leads to large-scale differences in water chemistry between the two islands, which have implications for stream periphyton development. In particular, much of the North Island has geology conducive to the release of phosphorus into waterways (Timperley 1983), leading to naturally high ambient DRP concentrations in many rivers. The potential for primary nitrogen limitation of periphyton growth in a subset of North Island rivers was highlighted by McArthur et al. (2010), by comparing observed ratios of DIN : DRP concentrations with the theoretical N : P content in nutrient-balanced phytoplankton (Redfield 1958).

3 Use of periphyton as an indicator of river ecosystem health

Two approaches have been applied to assess river ecosystem health using periphyton. The first is based on the quantity of benthic algae present, measured either as dry mass (or ash-free dry mass, a surrogate for total carbon), as chlorophyll *a* (the photosynthetic pigment present in all algae), or as estimates of periphyton cover on the stream bed. The rationale for this approach is that periphyton standing crop or cover exceeding certain levels can negatively affect both the appearance and recreational values of the waterway, and other components of the ecosystem (in particular invertebrates and fish) (Biggs 2000a, Suplee et al. 2009).

The second approach is based on taxonomic composition. A typical procedure is to document periphyton community composition across broad gradients of the water quality variables of interest (such as pH, DRP, NO₂-N, conductivity), then determine the water quality range associated with the highest abundance of each taxon. Scoring systems are then developed for the taxa (e.g., a high score for taxa associated with “good” water quality such as low nutrient concentrations, and low scores for taxa associated with “poor” water quality). Scores are then combined into a single index for each site (Kelly et al. 2008, Lavoie et al. 2014, Villeneuve et al. 2015). This assessment method indicates water quality only. The site scores are not linked to any instream values, but may be compared with a target score, such as a score representing the expected reference condition for the river of interest.

Regional differences in approaches to the use of periphyton to aid in river ecosystem assessments are highlighted below by comparing approaches in Europe and the USA with the approach in New Zealand. Overarching themes in all approaches are large uncertainties in understanding of how periphyton growth rates, standing crop and community composition are related to nutrient supplies (Page et al. 2012). This includes natural variability. Consequently large uncertainties in predictions of the effectiveness of management actions are to be expected.

3.1 Europe

In the European Water Framework Directive (WFD), European Union member states are required to assess the ecological status of rivers against a reference state (Kelly et al. 2012), using a combination of biological quality elements, which includes “phytobenthos”. In most countries the assessments include indices derived as described above from the taxonomic composition of periphyton, particularly diatoms. There is variation between countries (Besse-Lototskaya et al. 2011) but, in most cases, periphyton type is considered, but not quantity. Focusing on periphyton taxonomic composition avoids the issue of distinguishing between high abundance of periphyton that occurs naturally, or as a result of human-mediated eutrophication but at the cost of ignoring the detrimental effects that eutrophication-driven high abundance might have on recreational and aesthetic values in rivers (Kelly 2013). Consequently, the singular focus in the WFD on algal community metrics to assess river condition has recently been questioned (Kelly 2013), as has the reliability and utility of the metrics used (Demars 2013). There has been a recent call for inclusion of visual estimates of periphyton cover in river assessments to complement the taxonomic index approach (Kelly et al. 2016).

3.2 USA

In the USA, biomonitoring of freshwaters using periphyton has been applied for at least three decades, using both the quantity and index approaches. Development has included specification of standardised methods (Stevenson & Bahls 1999). Assessments of stream ecological health were initially carried out using data on periphyton chlorophyll *a* and community composition (particularly

diatoms), with the aim of developing composite indices of ecological integrity in different regions (e.g., Pan et al. 1999, Griffith et al. 2002, Hill et al. 2003, Stevenson et al. 2008). Large datasets accumulated in national sampling programmes were simultaneously used to develop nutrient criteria corresponding to baseline conditions of chlorophyll *a* (Dodds 2002, 2006, 2007). Phosphorus rather than nitrogen has been assumed to be the growth-limiting nutrient of most concern. Nevertheless, the role of N was recognised as early as 1990 (Elser et al. 1990), and calls for more emphasis on N as well as P have been made recently (Dodds & Smith 2016). Nutrient concentrations have been consistently measured as total nitrogen (TN) and total phosphorus (TP)², rather than dissolved nutrient concentrations, reflecting the long practice of using TN and TP to assess the trophic state of lakes (Carlson 1977).

3.3 New Zealand

Use of periphyton for assessing the ecological status of rivers in New Zealand has always been primarily based on quantity, either assessed as coverage of the stream bed or as chlorophyll *a* or ash-free dry mass (AFDM) determined as concentration per unit area (Biggs 2000b) and detailed protocols have been developed (Biggs & Kilroy 2000). Periphyton type has been included in broad terms by distinguishing cover by green filamentous algae (i.e., primarily chlorophytes) and mats (primarily cyanobacteria or diatoms). Cover assessments are still used in regional guidelines for the protection of river aesthetic and recreational values (e.g., Kilroy et al. 2016), and for national guidelines for the protection of human and animal health (Wood et al. 2009). The protocol document (Biggs & Kilroy 2000) includes a taxonomic guide to common taxa in New Zealand periphyton and methods for taxonomic sample analysis. However, no general indices relating periphyton to water quality have been developed, although good relationships between diatom community composition and water pH have been developed for small sets of streams (Schowe et al. 2013).

Since inclusion of periphyton abundance as an attribute in the NPS-FM (NZ Government 2014), measurements of chlorophyll *a* have become critical for assessing compliance.³ The issue of distinguishing between high abundance of periphyton that occurs naturally and high abundance as a result of human-mediated eutrophication is partly accounted for by identifying a subset of river sites as “naturally productive” (NZ Government 2014). Identification of such sites is from their climate and geology classes in New Zealand’s River Environment Classification (REC, Snelder & Biggs 2002).

An important feature of the NPS-FM is the requirement for monthly monitoring (see Section 4.2.1). This recognises that, in most rivers, peak biomass (as chlorophyll *a*) occurs only under certain conditions. However, regular occurrences of high enough chlorophyll *a* can affect river ecosystem health in the longer term (Biggs 2000b). Therefore the key to identifying whether periphyton is likely to be problematic is to identify the peak “carrying capacity” of the system, and the frequency of occurrence of those peaks. The levels of chlorophyll *a* defining the bands in the NPS-FM³ were set

² TN and TP are measures of the total amount of N and P in unfiltered samples. These total concentrations include both dissolved N and P and N and P assimilated into micro-organisms or bound to organic or inorganic particles and molecules. See Section 4.2.1.

³ For each attribute in the NPS-FM, a range of values is specified, in four bands from A (representing excellent ecological condition, or reference condition) to D (breaching a threshold determined to be the nationally acceptable “bottom line”). The periphyton bands are ≤ 50 mg m⁻² (A), $>50 \leq 120$ mg m⁻² (B), $>120 \leq 200$ mg m⁻² (C), and >200 mg m⁻² (D). The metric required for assignment of a river to a band is the 92nd percentile of monthly observations of chlorophyll *a*, based on at least three years of data. Thus, for a site to fall into band D, chlorophyll *a* would exceed 200 mg m⁻² in at least 3 of 36 monthly surveys. The narrative around the NPS-FM (Snelder et al. 2013) does allow for the use of other measures of periphyton abundance, provided that good relationships with chlorophyll *a* can be demonstrated. For example, visual estimates of cover on the stream bed can sometimes be converted to relatively accurate estimates of chlorophyll *a* (Kilroy et al. 2013).

based on effects on ecosystems (e.g., Biggs 2000b), and the requirement for three years of data recognised that occasional breaches of the thresholds are less damaging than frequent breaches.

A further requirement of the NPS-FM is that all regional councils in New Zealand are required to set water quality and quantity limits for freshwater management units (FMUs)⁴ in their region, where FMUs include both lakes and rivers. For lakes, the NPS-FM already specifies nutrient limits in terms of TN and TP. For rivers, the NPS-FM includes limits and guidelines for ammonium-nitrogen and nitrate-nitrogen, with levels set to manage for toxicity to aquatic organisms. However, uncertainties in relationships between nutrient concentrations and periphyton led to adoption of the direct measure of periphyton abundance (as chlorophyll *a*) as the only measure of ecosystem health in rivers. The negative effects of elevated dissolved nutrient concentrations on ecosystems (including periphyton proliferations) can occur at levels considerably lower than thresholds for toxicity-related effects on fish and invertebrates. National nutrient limits intended to manage for ecosystem health are still under discussion.

⁴ In the NPS-FM, a freshwater management unit is defined as “the water body, multiple water bodies or any part of a water body determined by the regional council as the appropriate spatial scale for setting freshwater objectives and limits and for freshwater accounting and management purposes” (NZ Government 2014).

4 Understanding periphyton in rivers: a primer

4.1 Terminology: growth vs. standing crop, growth vs. accrual

The topic of this review is periphyton **standing crop**. The review concerns the net amount of periphyton at sites of interest in rivers, at given times, which is the product of processes that lead to the accumulation of biomass (i.e., cell growth and division) and to the removal of biomass (e.g., from physical scouring, or grazing by invertebrates) (Figure 4-1). In subsequent sections of the review, where the terms periphyton **growth** or **growth rates** are used, they refer specifically to the rate at which algal cells grow and divide within periphyton. Growth rates are discussed only where it is considered necessary to refer to the basic processes of cell growth that contribute to standing crop, but do not necessarily control it. Similarly, the rate at which periphyton standing crop increases in rivers over time is referred to as the **accrual rate**, and is distinct from growth rate (Figure 4-1).

4.2 The role of nutrients in determining periphyton standing crop

Research into periphyton has been the subject of several recent reviews (Larned 2010, Furey & Liess 2013, Stevenson 2014), but the first comprehensive review was probably that presented in the edited volume *Algal ecology: freshwater benthic ecosystems* (Stevenson et al. 1996). A key message from that volume was an overarching concept of the main controllers of periphyton standing crop in streams (Figure 4-1). Put simply, the amount of periphyton on the stream bed at a particular site at a given time is a product of opposing processes that drive biomass growth and biomass loss (Biggs 1996).

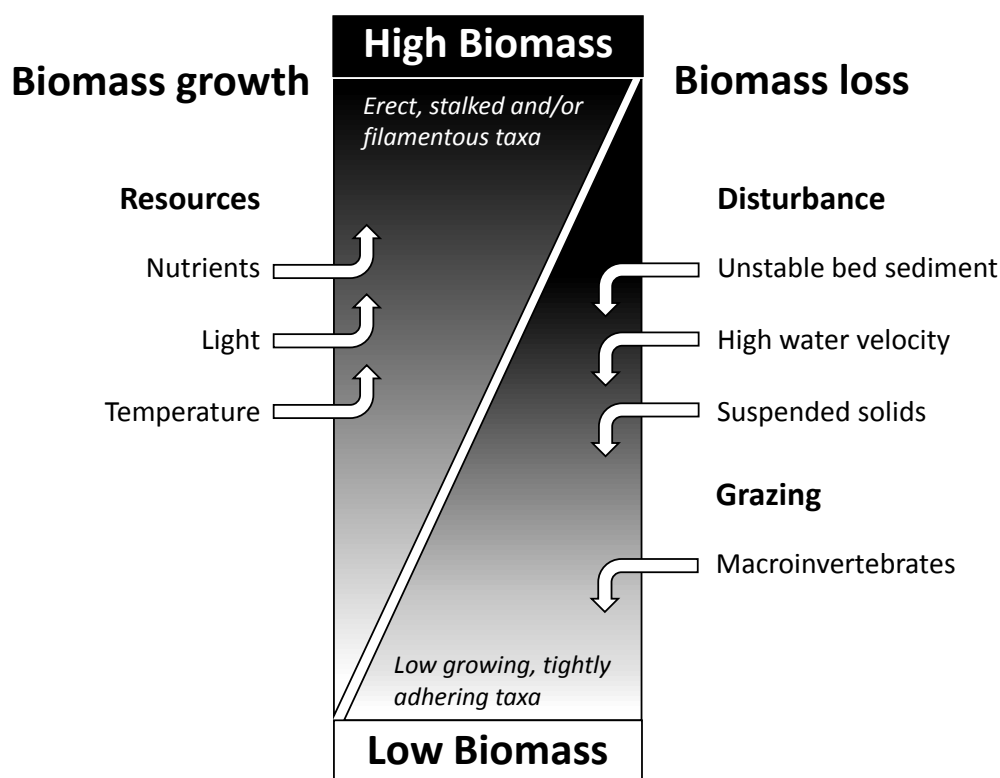


Figure 4-1: Conceptual model of processes that drive periphyton biomass growth and biomass loss, which together determine the rate of accrual. The relative strength of growth and loss processes may also influence the type of algae that dominates periphyton, shown at the low and high biomass extremes of the range (diagram adapted from Biggs 1996).

The fundamental requirements for growth of the algae in periphyton are nutrient supply and light. Assuming sufficient light is available for photosynthesis (see Section 7.2), algal cells cannot grow and divide unless sufficient nutrients are available. Once requirements for both nutrients and light are satisfied, then water temperature becomes important because temperature controls the rate of cellular growth processes (e.g., Bothwell 1988). The most important processes on the loss side of Figure 4-1 are disturbances (related to substratum type and stability, and flow variability) (Biggs 1995) and invertebrate grazing (Hillebrand et al. 2002). Interactions between both growth and loss processes and nutrient concentrations are discussed in Section 8. The role of disturbances in controlling periphyton standing crop has been the topic of extensive research in New Zealand (Biggs 1995, 1996, Biggs & Gerbeaux 1993, Biggs & Thomsen 1995, Biggs & Stockseth 1996, Biggs et al. 1999, 20005) and will be covered only briefly in this review.

Cell growth requires multiple nutrients in various amounts (Larned 2010), but the most important (i.e., required in the largest amounts) are carbon, nitrogen, phosphorus and silicon (for diatom cell structure). Carbon and silicon are generally present in rivers in supplies exceeding the maximum requirement for algal growth. However, in natural waters, nitrogen (N) and phosphorus (P) supplies can be low enough to constrain growth rates. In situations where a deficiency of N and/or P limits periphyton growth in streams, adding N and/or P will stimulate periphyton growth.

N and P limitation in periphyton has been thoroughly researched. Several reviews of the work have been completed (e.g., Francouer & Biggs 1999, Francouer 2001, Larned 2010, Keck & Lepori 2012) and will not be repeated here. The important point for the present review is that recent studies have concluded that focusing management efforts on either N or P, depending on which is identified as the periphyton-limiting nutrient, is a risky strategy. As an example, in North America, over the last few decades, phosphorus has generally been assumed to be the main driver of periphyton proliferations (Dodds 2003a). However, the latest advice emphasises that both N and P influence stream eutrophication, and both need to be considered (Dodds & Smith 2016). In New Zealand, simultaneous management of both N and P has been advised since at least 2007 (Wilcock et al. 2007).

The emphasis on N and P management for controlling periphyton growth is supported by the results of many experimental studies since the 1970s that have shown that, assuming that growth rates are not already maximum, addition of nutrients (N and P) to algal cultures or communities stimulates growth rates (reviewed by Borchardt 1996). Whether this known effect of nutrient enrichment on algal growth rates (subject to the assumption of initially nutrient-limited growth) translates into increases in standing crop is the topic of later sections in this review.

4.3 Linking periphyton standing crop to nutrients

4.3.1 Use of time-series data

While the important role of nutrients in determining periphyton **growth rates** can be clearly demonstrated in controlled, manipulative experiments (Borchardt 1996), demonstrating that role in the natural habitat of rivers is more difficult than in experiments. One reason for the difficulty is that, in rivers, processes causing loss of algal cells occur at the same time as cell growth and division. Therefore, net standing crop of periphyton at a given time depends on all of the processes (Figure 4-1), and a measurement of standing crop made at a particular time will rarely directly reflect nutrient concentrations at that time. When developing relationships between periphyton and nutrient concentrations, one way to minimise the influence of other controlling factors is to use time

series of periphyton data (e.g., from monthly sampling over at least a year) in conjunction with time-series of nutrient concentrations. The time series allows identification of maximum values or calculation of high percentiles (e.g., 95th percentile) of periphyton, which are more likely to be linked to average availability of nutrients. Maxima in a time series may represent the carrying capacity of the site, and consequently are more likely to be related to the limiting factor for peak or nuisance conditions. Identification of maximum standing crop (as chlorophyll *a*) was the rationale for the requirement for time-series monitoring in the NPS-FM (see footnote 3, Section 3.3). The effect of using single samples (i.e., synoptic surveys) versus time-series data is discussed in Section 7.2.

An exception to the general rule that maximum values of periphyton standing crop extracted from time series data are most likely to reflect averaged nutrient concentrations occurs when samples are taken along gradients of nutrient concentrations in the same river. Sampling along rivers removes some of the variability in site characteristics between rivers. If sites are selected with similar physical characteristics (e.g., shade, bed substrate composition, water velocity) then responses to differences in nutrient concentrations are often clear (see Section 7.1).

4.3.2 Sampling periphyton

A second difficulty in relating periphyton standing crop to nutrient concentrations relates to sampling technique. Unless samples are collected from appropriate habitat and with sufficient subsamples to account for spatial variability of periphyton on the stream bed, the resulting data cannot be expected to reflect nutrient supply.

Detailed protocols for periphyton sampling in New Zealand streams were set out in Biggs & Kilroy (2000). Two important guidelines are:

1. Runs, rather than riffles, are advised as most appropriate for periphyton monitoring. Runs are defined as having smooth water flow with an unbroken surface, with variable water velocity, but generally slower than in riffles. Riffles, on the other hand, are defined by shallow, faster-flowing turbulent water and stable substrata. Reasons for focusing on runs are:
 - runs are the most common habitat type in most rivers;
 - standardising the habitat to runs means that application of guidelines such as the NPS-FM are nationally consistent;
 - periphyton standing crop in runs tends to be more variable over time and more responsive to the effects of both high flows and nutrient supply than that in riffles. Riffles tend to support persistent high standing crop because: (a) riffles by definition have stable substrata; and (b) higher water velocities, rather than nutrient concentrations, control nutrient uptake rates (Larned et al. 2010), so that high biomass can occur even when nutrient concentrations are low.
2. Within each run, multiple samples need to be collected (e.g., on transects in wadeable depths) to ensure that the combined sample integrates periphyton from the range of depths and water velocities at the site (e.g., Kilroy et al. 2013).

The sampling guidelines set out by Biggs & Kilroy (2000) remain applicable. Updated guidelines specifically relating to the NPS-FM periphyton attribute are under development.

5 Variability in nutrient supplies to periphyton

Catchment development for urbanisation or agricultural production typically leads to additions of either or both of N and P to the landscape, and eventually to waterways (Wilcock et al. 2013). In rivers and streams, the major supplies of N and P to periphyton are generally assumed to originate in the overlying water. However, once a layer of periphyton grows more than a thin layer of cells, internal recycling processes within the mat may start to uncouple periphyton growth rates from that expected based on nutrient supplies from the water column (Dodds 2003b, Mulholland & Webster 2010). Furthermore, differences between N and P in their availability, chemical behaviour and transformation processes (cycling) lead to contrasting patterns in instream dynamics and their relationships with periphyton growth and standing crop.

In this section, the processes of nitrogen and phosphorus cycling in rivers are described as background to understanding variability of N and P supplies in rivers.

5.1 Nitrogen cycling

5.1.1 Measures of nitrogen

Nitrogen occurs naturally in freshwaters as soluble oxidised forms (nitrate-N, or $\text{NO}_3\text{-N}$; and nitrite-N, $\text{NO}_2\text{-N}$), reduced form (ammoniacal-N, $\text{NH}_4\text{-N}$), and in organic forms. In river waters, oxidised nitrogen is dominated by $\text{NO}_3\text{-N}$, which is measured in the laboratory using the cadmium reduction method. Ammoniacal N ($\text{NH}_4\text{-N}$) is usually present as a small proportion of dissolved inorganic N and is measured separately. Concentrations of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ are often combined to provide an estimate of dissolved inorganic nitrogen (DIN) (e.g., Keck & Lepori 2012).

Organically bound N is also present in freshwaters. Total dissolved nitrogen (TDN) is defined operationally as the N extracted using persulfate oxidative digestion on samples filtered through 0.45 μm membrane filters. Dissolved organic nitrogen (DON) is defined as TDN minus DIN. TDN is not measured routinely in many New Zealand rivers, as DON is assumed to be largely biologically unavailable. However, compounds such as urea may be taken up by some algae (Donald et al. 2013). Total nitrogen (TN) is measured in the same way as TDN, but using unfiltered samples. TN therefore includes N from all organic material in the sample, including organisms, as well as DIN.

5.1.2 Nitrogen sources and processing

Nitrogen is a component of cellular proteins, nucleic acids and other biomolecules. N is abundant in the environment, making up almost 78% by volume of the atmosphere as gaseous N_2 . Only organisms with the ability to fix nitrogen can use N_2 directly. In general, nitrogen is available to periphyton as $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, and possibly in low molecular weight organic form (DON, e.g., Sundback et al. 2011, Donald et al. 2013). Available N in headwater streams can be dominated by $\text{NH}_4\text{-N}$ but supplies of N in rivers in general are usually dominated by $\text{NO}_3\text{-N}$. The small proportions and loads of $\text{NH}_4\text{-N}$ in waterways are generally taken up rapidly by primary producers (i.e., periphyton) and or converted to $\text{NO}_3\text{-N}$ through nitrification (Figure 5-1).

Nitrogen is naturally available in rivers from rainfall (Timperley et al. 1985), catchment seepage (Peterson et al. 2001a, Wetzel 2002) and recycling (remineralisation) of plant material and decaying algae (Wetzel 2002) (Figure 5-1). The presence of N-fixing vegetation in stream catchments has been linked to elevated export of N to streams in the USA (Compton et al. 2012), leading to increases in periphyton chlorophyll *a* in some cases (Wiegner et al. 2013). Such increased N-leaching likely occurs in New Zealand in areas infested by invasive legumes such as gorse (Drake 2011, Hamill et al. 2012).

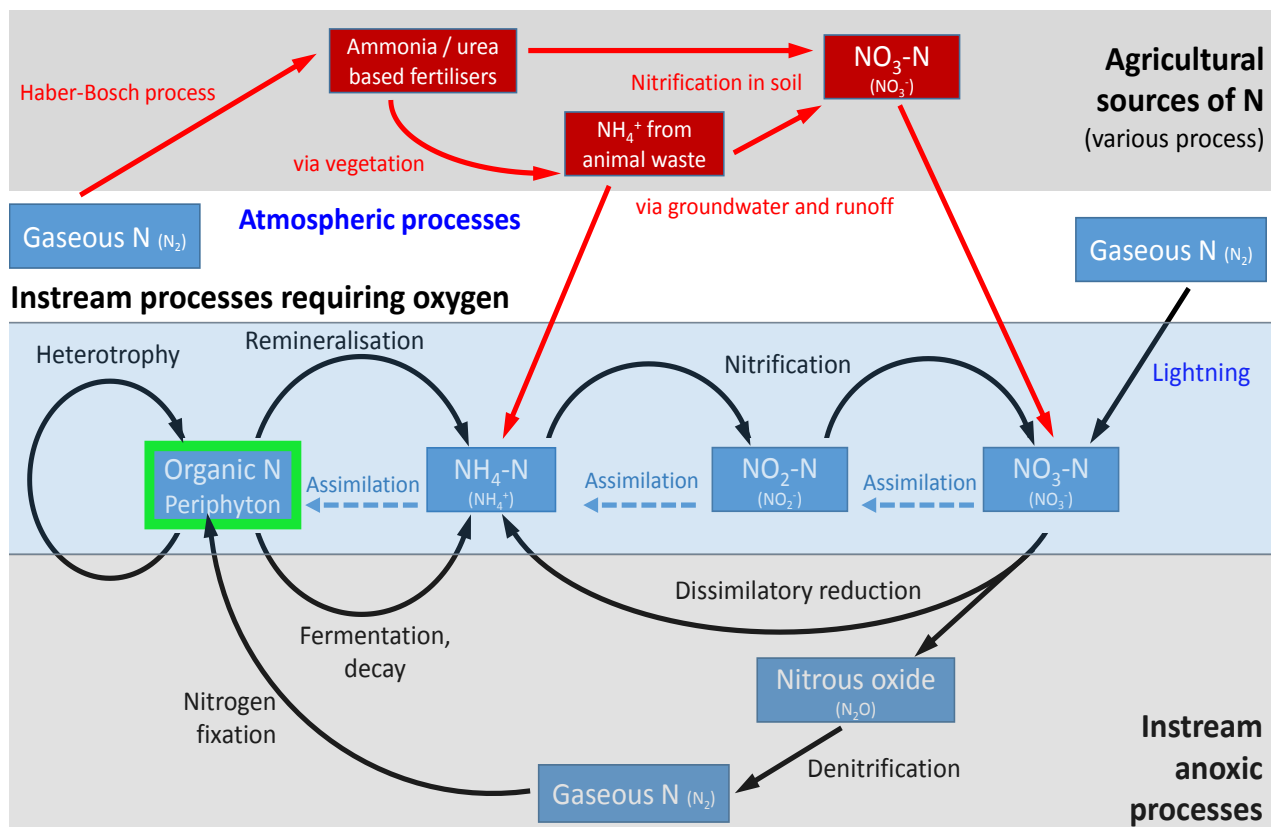


Figure 5-1: Simplified diagram of the nitrogen cycle in streams including potential inputs from agriculture. Blue boxes and black arrows denote natural sources and processes. Red boxes and arrows denote anthropogenic processes and sources. Adapted from Dodds (2002).

Denitrification (Figure 5-1) refers to a process that occurs in anoxic conditions in waterways, mainly within the sediments, in which $\text{NO}_3\text{-N}$ is reduced to gaseous N_2 , mediated by denitrifying bacteria. In terms of remediating high periphyton growth rates, denitrification is of particular interest because this is the only process in which N is permanently removed from a river system. Denitrification reverses (a) nitrogen fixation by some cyanobacteria and terrestrial plants; and (b) the Haber-Bosch process that has allowed manufacture of $\text{NH}_4\text{-N}$ from N_2 on an industrial scale to produce agricultural nitrogen fertilisers (Erisman et al. 2008).

The process of denitrification requires a supply of NO_3^- , anoxic conditions, a source of organic carbon, and the presence of bacteria capable of mediating the process (Birgand et al. 2007). These conditions are rarely, if ever, met in flowing stream water, but can be met within biofilms (i.e., periphyton) attached to stream sediments, and within the sediments. Denitrification rates can be particularly enhanced in zones of vertical hyporheic – surface water exchange (Gomez-Velez & Harvey 2014). For example the potential for removal by denitrification of up to 10% of a stream’s nitrate in a 100-m groundwater – surface water mixing reach has been demonstrated (Harvey et al. 2013). Rates of denitrification in sediments depend on the concentration of NO_3^- in the overlying water and on nitrification of $\text{NH}_4\text{-N}$ in the surface sediments (Birgand et al. 2007). Denitrification rates are higher in warmer temperatures (reviewed by Birgand et al. 2007). Benthic fauna such as worms can increase denitrification rates through facilitating diffusion of NO_3^- through the sediments to denitrifying sites (Chatarpaul et al. 1980).

5.2 Phosphorus cycling

5.2.1 Measures of phosphorus

Phosphate is measured in the laboratory as dissolved reactive phosphorus (DRP),⁵ which is defined operationally as the fraction quantified by the phosphomolybdic acid methodology using samples filtered through 0.45 µm membrane filters (Jarvie et al. 2002). It has long been recognised that the standard laboratory method for measuring DRP overestimates PO_4^{3-} concentrations, because it also picks up a proportion of organically bound P (Rigler 1962, Whitton & Neal 2011). Therefore laboratory measures of DRP should be thought of as the maximum PO_4^{3-} in a sample.

The total quantity of organic P in a filtered sample is measured using the same method as for DRP, but following persulfate digestion. This fraction is termed total dissolved phosphorus (TDP) and includes organically bound P. Total phosphorus (TP) is determined using the same analytical method as TDP, but on an unfiltered sample. Dodds (2003) argued that, because of the uncertainties around the analysis method, DRP is a very poor measure of bioavailable P in streams, and TP is a much more accurate indicator of eutrophication. However, high proportions of TP can be delivered during storm flows, only small proportions of which are bioavailable (Ellison & Brett 2006).

In New Zealand DRP and TP are measured at many river sites, but TDP is rarely measured routinely. TDP may better represent the fraction of bioavailable P in many streams because, when phosphate is in short supply, most algae can release phosphatases, enzymes that enable release of phosphate from organic molecules (Ellison & Brett 2006, Whitton & Neal 2011).

5.2.2 Phosphorus sources and processing

The phosphorus requirements of primary producers are much lower than those for nitrogen. Phosphorus is generally bioavailable only as phosphate ions, PO_4^{3-} , which are taken up rapidly by instream biota (Hall et al. 2013). Phosphate is very reactive and combines readily with inorganic particles, through adsorption, or into complexes with metals such as iron (Fe) or calcium (Ca), into biologically unavailable forms (Dodds 2003; Withers & Jarvie 2008). Under certain chemical conditions (anoxia, or high pH) phosphate can be re-released from these complexes, and, in some circumstances, can become directly available for uptake within periphyton mats (see Section 8.1).

Phosphorus is recycled within streams through processes that facilitate either binding of PO_4^{3-} molecules to inorganic sites, or the release of PO_4^{3-} from those sites (Figure 5-2). Natural sources of P to waterways include transport on soil or dust particles, and microbial breakdown of leaf litter and other organic matter (Withers & Jarvie 2008). In the Northern Hemisphere, substantial instream P may derive from annual fish migrations (Harding et al. 2014), but such a source is minor in New Zealand.

Phosphorus sourced from agricultural practices includes that from fertilizers and manure. Because phosphorus binds readily to mineral and organic particles, most P losses to streams and rivers are via direct runoff in particulate form. DRP may also leach to groundwater in agricultural catchments when the capacity of soils to hold P is exceeded (McDowell et al. 2015).

⁵ also called filterable or soluble reactive P (FRP, SRP)

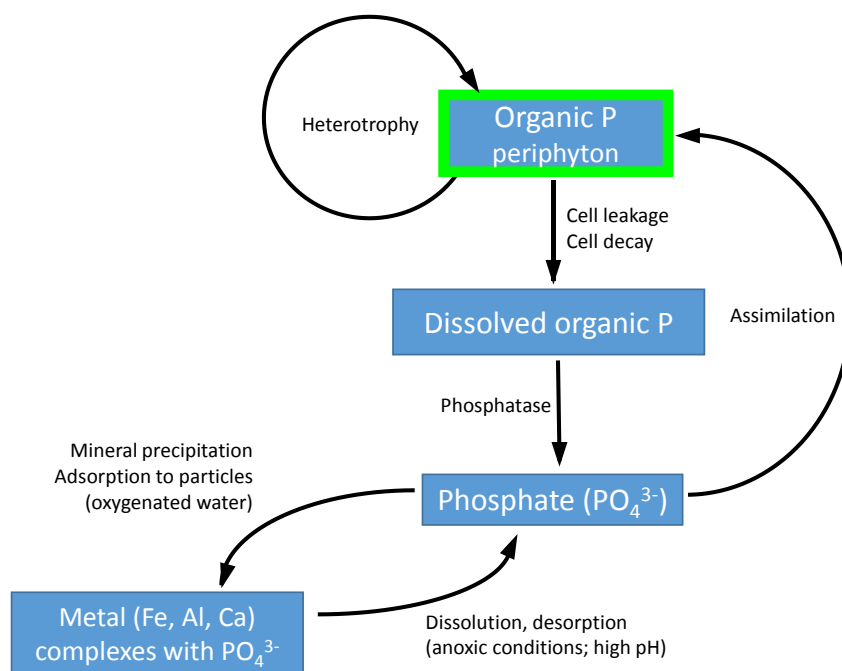


Figure 5-2: Simplified diagram of phosphorus cycling in streams. Note that unlike the nitrogen cycle, there is no gaseous phase in the cycling of phosphorus. New P is added to the cycle via organic, inorganic and bound phosphorus, through leaching or from direct deposition into waterways. Adapted from Dodds (2000).

5.3 Longitudinal patterns in nutrient concentrations

5.3.1 Nutrient spiralling

Transport and uptake of nutrients along streams is encapsulated in the nutrient spiralling concept (Ensign & Doyle 2006). Nutrient spiralling refers to the way in which “parcels” of nutrient (N or P) molecules travel down a river continuum in successive states of availability (as dissolved ions) and non-availability (through being incorporated into biological molecules or lost by some other process). Inputs of nutrients along a river continuum, from diffuse leaching, groundwater, tributaries or point-source discharges, interact with the spiralling process. Spiralling is a way of describing the N and P cycle, discussed above (see Figure 5-1, Figure 5-2) in the context of the downstream water flow in rivers.

Contributors to nutrient usage (or loss) in streams include: uptake (assimilation) by benthic and planktonic algae, uptake by macrophytes, denitrification (see Section 5.2.2 above), adsorption of phosphate ions onto inorganic and organic particles. All these processes contribute to **uptake rates** (see Section 5.4.2).

The spiralling behaviour of nitrogen and phosphorus differ in that nitrogen uptake rates are generally higher than those for phosphorus because of the much higher biological demand. The capacity of P to bind to particles or form relatively stable complexes with metals leads to faster spiralling process compared to that of N (Ensign & Doyle 2006). In their review of phosphorus processing, Withers & Jarvie (2008) concluded that “the capacity to retain (process) P within the river channel, and hence regulate the downstream delivery of P without stressing the aquatic communities present, is considerable, especially in headwaters.”

5.3.2 Measures of nutrient removal

The direct measure of nutrient (i.e., N or P) usage is removal from the water column as weight of N or P per unit area of riverbed per unit time (e.g., $\mu\text{g m}^{-2} \text{s}^{-2}$), known as the **uptake rate (U)**. The theory of nutrient spiralling has led to two further useful measures representing nutrient usage in waterways: uptake length and uptake velocity (Dodds et al. 2002). **Uptake length (S_w)** is the distance between entry of a molecule into a river reach and its removal from the water column through assimilation or other process. The distance can be measured by using radioactive tracers or by tracking attenuation of direct nutrient additions (Mulholland 2010). The two measurement methods do not provide exactly equivalent results: tracers measure the **total uptake rate** of removal of N from the water column by any process; additions allow measurement of **net uptake rate** and cannot account for return of molecules the water column by recycling processes.

Uptake velocity (v_i) refers to the speed at which an ion is removed from water. It is a measure of uptake efficiency by taking account of water velocity and depth. Uptake velocity reflects demand relative to supply. For example, a large, deep river with high background N or P concentrations would be expected to have relatively low uptake velocities; whereas in a small, shallow stream with moderate N or P concentrations, uptake velocities would be high. Uptake velocity should be constant across a range of non-saturating uptake rates, but should decline as nutrient concentrations increase beyond the saturating range, because there are so many molecules available compared to uptake requirements (Dodds et al. 2002).

5.3.3 Controllers of nutrient removal

Patterns of nutrient concentrations within a river network, from low-order, small streams to high-order rivers, can be explained by the processes that drive U, especially benthic primary production (i.e., periphyton). Uptake rates vary with concentrations in the overlying water. Biologically driven uptake (i.e., by periphyton) will also vary with temperature and light.

Nutrient concentrations and stream size: Nitrogen removal has been shown to increase with $\text{NO}_3\text{-N}$ concentrations at least up to about 700 mg m^{-3} (Dodds et al. 2002). At some concentration above this, uptake would be expected to saturate, but this value may vary depending on the processes dominating uptake. For example, uptake rates may be particularly high in the presence of green filamentous algae, which present a large surface area for uptake (Dodds et al. 2002).

At uniform, low to moderate N concentrations, NO_3^- and NH_4^+ uptake length increases with river size, reflecting the larger water volume relative to river bed area in larger rivers, but uptake velocities remain constant (Wolheim et al. 2006). Peterson et al. (2001) showed how headwater stream water (with DIN concentrations $< \sim 100 \text{ mg m}^{-3}$) can use over half of N inputs through assimilation by periphyton and removal by denitrification, thereby controlling N export downstream (see also Alexander et al. 2000). However, N export from headwaters with more catchment development can account for large proportions of N in higher order streams and rivers (70% in second-order streams and up to 55% in rivers larger than fourth order) (Alexander et al. 2007).

The concentrations of $\text{NO}_3\text{-N}$ in streams in agricultural landscapes can be orders of magnitude higher at downstream sites than in headwaters. Under these conditions (e.g., DIN concentrations $> \sim 1500 \text{ mg m}^{-3}$), assimilation by periphyton tends to predominate over denitrification (Arango et al. 2008); both assimilation and denitrification consume a very small proportion of the nitrogen passing over a reach and most is exported downstream (Mulholland et al. 2008, Martin et al. 2011).

Season, temperature and light: In field experiments in Otago streams, nutrient uptake was shown to vary throughout the year but net uptake rates of NO_3^- , NH_4^+ and DRP were not correlated with any seasonal environmental variable (Simon et al. 2005). In experiments in the North Island, net uptake rates of NO_3^- and TDN in full light were higher during spring and summer than during autumn or winter. No net uptake of DRP or TDP was detected during the daytime, but TDP was taken up during the night in spring (Matheson et al. 2012).

Changes in light availability that affect nutrient uptake rates as headwater streams leave forested areas can lead to unexpected outcomes in downstream nutrient concentrations. In a summer study in a largely unimpacted catchment, dissolved phosphorus (measured as TDP) declined as stream order increased, particularly at the transition from catchments $<100 \text{ km}^2$ to $>100 \text{ km}^2$; this was attributed to increased assimilation (uptake) by periphyton in the larger streams, especially where light ceased limiting growth at the transition from small, incised forested streams to larger, more open rivers (Finlay et al. 2011). In contrast DIN was low ($<15 \text{ mg m}^{-3}$) throughout the network, and N:P ratios up to 4 suggested strong N limitation of periphyton growth⁶ in the upper catchment. However dissolved organic N increased approximately five-fold at the $>100 \text{ km}^2$ catchment area threshold, leading to potential P-limitation in downstream reaches. The source of the DON was suggested to be recycled material from algal growth in the larger rivers (where light was not limiting), which relied on the fixation of atmospheric N as a nitrogen source. Thus N was being added to this naturally low-DIN system in a downstream direction, even without human impacts, although in organic form.

Increases in organic N concentrations over time, and coinciding with measurable uptake of NO_3^- and NH_4^+ have also been documented in experimental channels (Matheson et al. 2012). In that case release of organic N was unrelated to season, and was attributed, at least in part, to heterotrophic metabolism (e.g. microbial decomposition).

Water velocity: Larned et al. (2004) demonstrated experimentally that uptake rates of both N and P, standardised to chlorophyll *a*, were proportional to water velocity, in starting conditions of 200 mg m^{-3} DIN and 15 mg m^{-3} DRP. The Larned et al. (2004) findings were corroborated in a field experiment in which growth on artificial substrata was tracked in five velocities in nutrient-enriched and control treatments. A positive response by periphyton chlorophyll *a* to current velocity (up to 1 m s^{-1}) was accentuated by nutrient additions, even though the N and P additions were very low (Townsend et al. 2012).

Drivers of uptake length: Uptake length depends on nutrient concentrations up until nutrient concentrations reach saturating levels (i.e. a maximum uptake rate, Bernot et al. 2006), river flow volume, water depth, water velocity and rate of uptake of N and P. In small oligotrophic streams, uptake lengths can be very short because demand relative to supply is low, and available molecules are taken up rapidly. Conversely, in eutrophic streams, uptake lengths are longer because so many molecules are available for uptake. Uptake lengths can be infinite (i.e., unmeasurable) in large eutrophic waterways.

Relationships between uptake and chlorophyll *a*: While there is considerable literature on uptake processes in waterways, few studies were located in which uptake rates were compared with or

⁶ Likely nutrient limitation determined from DIN:SRP ratios, based on the Redfield ratio of 16N : 1P (by atoms, equivalent to 7N : 1P by weight) observed in marine phytoplankton (Keck & Lepori 2012). As a general rule, ratios between say ~ 20 and ~ 5 (by weight) are inconclusive (Francouer et al. 1999). N : P > 20 usually indicates P limitation, and N : P < 5 , N-limitation. The range of uncertainty could be even broader (Keck and Lepori 2012).

related to periphyton standing crop. A positive relationship between NO_3^- uptake and chlorophyll *a* was detected in one Otago stream (Simon et al. 2005). Lack of correlation in other streams was likely because standing stock of chlorophyll *a* is the product of both growth and removal processes of algae (see Section 4). In addition, other factors could influence uptake rates. For example, the presence of wood in streams has been suggested to promote N removal by denitrification (Ensign & Doyle 2005), and this could have a seasonal component. Subsequent experiments have not always corroborated this potential role for wood (e.g., Warren et al. 2013).

Larned et al. (2004) used uptake rates normalised to chlorophyll *a* in experiments focussed on the effects of water velocity on uptake, but did not report any direct relationship between chlorophyll *a* concentration and uptake rate. However, in a streamside experiment, uptake per unit area and demand (equivalent to v_f , see Section 5.3.2 above) for NO_3^- , DRP, TDN and TDP were all positively related to chlorophyll *a*. (Matheson et al. 2012). This supported findings in other studies that autotrophic production often accounts for a large proportion of nutrient removal in streams (e.g., Arango et al. 2008).

5.4 Temporal patterns in nutrient concentrations

Nutrient inputs to waterways are controlled by catchment conditions (i.e., nutrients available at a given time, driven by terrestrial processes and temperature) and climate (rainfall patterns) (Bernot et al. 2006), which change over time in predictable and unpredictable ways at scales varying from days (diurnal variation) to years. Rainfall patterns are responsible for some of the temporal variability seen in nutrient concentrations across days to seasons. Flushes of nutrients raise concentrations during storm flows, and minimal runoff causes inputs (and therefore concentrations) to decline during periods of low flows (Hall et al. 2009). The contributions of groundwater to river water vary with flow volume. Therefore, groundwater can be the source of large seasonal fluctuations in nitrate to the extent that concentrations are very high in winter high flows and extremely low in summer low flows (Woodward et al. 2013). Nitrogen-fixing vegetation in the catchment may also contribute to N-leaching, with seasonal peaks in autumn (Magesan et al. 2012).

Instream nutrient concentrations are also affected by processes that are independent from flows. The typical seasonal pattern of DIN in streams is maximum concentrations from late autumn to early spring (the dormant season) and minimum concentrations in summer (season of maximum terrestrial biological uptake, and lower runoff rates) (Goodale et al. 2009). Here, the “dormant season” refers to mainly to low growth rates of terrestrial plants and periphyton in low winter temperatures. Low plant growth rates reduce terrestrial uptake of nutrients, leading to increased concentrations in runoff. The effect is exacerbated because runoff may also be higher at that time of year, especially during spring snowmelt. Brief increases in $\text{NO}_3\text{-N}$ concentrations can be caused by microbial breakdown of leaf litter in autumn (Goodale et al. 2009), and some waterways display summer maxima in $\text{NO}_3\text{-N}$ concentrations, stimulated by processes within catchment soils (Goodale et al. 2015), or groundwater inputs during summer low flows (Mulholland & Hill 1997, Bernal et al. 2015).

Phosphorus concentrations can show similar regular seasonal fluctuations. The drivers of seasonal patterns include temperature-mediated differences in instream uptake (Mulholland 2004), and hydrological control through flushing of P following accumulation in catchments during the dry season (Vink et al. 2007).

An overview of seasonal patterns in DIN and DRP concentrations in New Zealand rivers is provided in Section 6.

6 DIN, DRP and periphyton cover in New Zealand rivers

Data on DIN and DRP are routinely obtained by regional councils and NIWA from hundreds of sites throughout New Zealand (Larned et al. 2016). The NRWQN comprises 77 of those sites. Although the sites in the NRWQN are not necessarily representative of all river types in New Zealand, the dataset is the longest available (monthly data collection since 1989), and sample collection and analysis methods have remained consistent over the entire record (Davies-Colley et al. 2011). The sites are all in relatively large rivers, but include Hill and Mountain Rivers (as defined in Section 2), most of which have cobble beds that support periphyton rather than macrophytes. The dataset includes sites with largely unimpacted catchments (termed **Baseline sites**) and sites with developed catchments (termed **Impact sites**). DIN and DRP data from the NRWQN sites from 2006 to 2015 were used to summarise spatial and temporal patterns in New Zealand in relation to broad land use, and differences between the North and South Islands.

Periphyton data are available for all NRWQN sites, as estimates of percentage cover by filaments and mats at each site on each survey date. These estimates were used in a preliminary evaluation of the differences in periphyton cover between islands and river type (Baseline vs. Impact). Mean cover and the 92nd percentile of cover were calculated for each site over the period 2006 to 2015.

6.1 Spatial patterns

The natural (i.e., pre-human) concentrations of DIN in New Zealand rivers were probably very low. Even at present, NRWQN sites classed as Baseline have mean DIN well over an order of magnitude lower than at Impact sites (Table 6-1). Natural concentrations of DRP also appear low, although the difference in concentrations between baseline sites and impacted sites is much lower than for DIN, with impacted sites having, on average just three times the DRP concentration of baseline sites (Table 6-1). These data also highlight higher mean DRP at North Island sites than South Island sites, across all classes of impact, while differences for DIN are minor between islands. Naturally high DRP in the central North Island in particular is attributable to the particular type of volcanic geology in the area, which results in water chemistry that facilitates release of P into the water column rather than its incorporation into stable complexes that are not bioavailable (Timperley 1983).

Estimates of reference condition for NO₃-N, NH₄-N and DRP in New Zealand, using a much larger dataset of >1000 sites showed variation across classes in the River Environment Classification (REC) with highest reference values in lowland streams and in streams in the warm climate category (McDowell et al. 2013).

6.2 Seasonal patterns

Seasonal patterns in DIN were detected at 90% of the 77 sites in the NRWQN (Table 6-2). With few exceptions, the months of peak concentrations were July and August and lowest concentrations February and March.

In the North Island, at 34 of the 40 sites showing seasonal patterns there was also a significant positive correlation between discharge at the time of sample collection and DIN, suggesting that the seasonal pattern was at least partly driven by flow (Table 6-2). In the South Island DIN and flow were strongly correlated at fewer sites (16 of 30 sites). There was a significant negative correlation between DIN and flow at three sites, indicating that the high flows carrying low DIN concentrations originated in pristine upper catchments (Table 6-2).

Table 6-1: Summary of mean and median concentrations of DIN and DRP at sites in the NRWQN. Data used were from 2006 to 2015. Units are mg m⁻³. Standard deviations are shown in parentheses. The three land use categories are based on the Baseline or Impact status assigned to each NRWQN site in 1989 (Davies-Colley et al. 2011). The Partly impacted class includes sites originally placed in the Baseline category, but whose REC landcover class is P (pasture). Refer to Table 4-3 for *n* in each site category by island.

Site category	Statistic	All sites (<i>n</i> = 77)		North Island (<i>n</i> = 44)		South Island (<i>n</i> = 33)	
		DIN	DRP	DIN	DRP	DIN	DRP
Baseline (<i>n</i> = 22)	Mean (s.d)	29.4 (22.9)	3.9 (4.7)	32.7 (27.0)	6.6 (6.0)	26.6 (19.7)	1.6 (0.9)
	Median	29.8	2.3	31	4.2	26.4	1.4
Partly impacted (<i>n</i> = 10)	Mean (s.d)	250 (179)	5.4 (2.7)	222 (117)	6.4 (2.9)	294 (262)	4.0 (2.0)
	Median	249	5.2	249	6.8	254	4.1
Impact (<i>n</i> = 45)	Mean (s.d)	342 (393)	10.9 (12.5)	355 (385)	14.8 (14.4)	320 (416)	4.3 (3.4)
	Median	169	6.7	218	10.0	137	3.3

Table 6-2: Percentages of sites in the NRWQN with and without seasonal patterns and correlations with flow, for DIN and DRP. Numbers of sites are in parenthesis, in italics. Data used were from 2006 to 2015. Seasonal patterns were identified from non-parametric Kruskal-Wallis tests in which DIN and DRP differed significantly across months over the 10-year period, and where the seasonal pattern was evident from plots of the raw data by month. Correlations with flow were identified from a Pearson correlation matrix generated for each site using log-transformed data. Significant relationships had $R > 0.30$ ($P < 0.05$). R was well over the threshold of 0.3 at most sites.

Island	Significant correlation with flow	Percentage of sites with seasonal patterns (<i>n</i>)			
		DIN		DRP	
		yes	no	yes	no
North (<i>n</i> = 44)	yes	77.3 (34)	0.0 (0)	54.5 (24)	29.5 (13)
	no	13.6 (6)	9.1 (4)	6.8 (3)	9.1 (4)
South (<i>n</i> = 33)	yes	48.5 (16)	3.0 (1)	21.2 (7)	54.5 (18)
	no	42.4 (14)	6.1 (2)	6.1 (2)	18.2 (6)

DRP differed from DIN in that smaller proportions of sites in both islands showed seasonal patterns in DRP (Table 6-2). In the North Island, DRP was correlated with discharge at the time of sampling at two thirds of the 44 sites, and most (>90%) showed seasonal patterns in DRP. The correlations with discharge were negative at five sites. At least three of these sites have known point-source discharges upstream.

In the South Island, less than one third of the sites showed seasonal patterns in DRP and most of these sites also showed positive correlations between DRP and discharge. The one site with a negative correlation was downstream of a wastewater treatment plant.

The months of peak DRP concentrations were usually July and August in the North Island. In the South Island, peak DRP began in June at seven sites, with minima from December to March. One site had maximum DRP in April, and minimum in October; and a further site had highest DRP in December to January, and minimum values in July. The latter two sites were in the Taieri catchment, which has unusually high DRP values compared to many other South Island rivers.

In summary, the seasonal patterns in DIN and DRP concentrations seen in many rivers are likely to be largely related to seasonal flow patterns. However, many rivers (especially in the South Island) showed seasonal DIN but no relationship to flow, indicating that other processes (including catchment and instream uptake) drove temporal changes in DIN (Bernot et al. 2006, Hall et al. 2009, Goodale et al. 2009). DRP differed in that many sites (both islands) showed no seasonal pattern, although the concentrations were correlated with flow. Most correlations with flow were positive (suggesting runoff effects), but at sites downstream of point-source discharges, the correlations tended to be negative.

6.3 Periphyton percentage cover

The N and P concentrations in New Zealand rivers indicate that periphyton at Baseline sites in the North Island rivers would be expected to be generally nitrogen limited, and in the South Island more likely to be phosphorus limited, or possibly co-limited by both N and P.⁷ Therefore there would be no clear expectation of higher periphyton cover in either island. In fact, cover was variable in both islands (shown by the large standard deviations compared to the means in Table 6-3). Cover by filaments did not differ between islands in any of the three site categories (Mann-Whitney U-tests, $P > 0.3$ in all cases). However, mean cover by mats was higher at Baseline sites in the South Island than in the North Island, because many South Island sites were affected by *Didymosphenia geminata* (didymo) (Kilroy & Bothwell 2102).

Table 6-3: Summary of mean and 92nd percentile of percentage cover by periphyton (filaments and mats) at sites in the NRWQN. Data are from 2006 to 2015.

Island	Site category	Statistic	Mean % cover		92 nd percentile % cover	
			Filaments	Mats	Filaments	Mats
North	Baseline (<i>n</i> = 10)	Mean (s.d)	4.1 (6.2)	3.1 (4.6)	11.4 (17.2)	9.7 (14.6)
		Median	1.0	1.0	2.0	1.3
	Partly impacted (<i>n</i> = 6)	Mean (s.d)	6.7 (6.3)	5.5 (4.2)	23.0 (22.0)	22.1 (17.3)
		Median	6.8	5.2	22.4	22.6
	Impact (<i>n</i> = 28)	Mean (s.d)	9.9 (9.3)	6.1 (6.7)	31.8 (25.2)	20.2 (19.0)
		Median	7.1	5.6	24.2	21.5
South	Baseline (<i>n</i> = 12)	Mean (s.d)	2.8 (3.7)	12.9 (17.3)	7.9 (9.5)	31.6 (33.9)
		Median	1.4	5.4	4.2	21.0
	Partly impacted (<i>n</i> = 4)	Mean (s.d)	4.6 (4.3)	12.3 (18.8)	16.7 (20.8)	30.0 (40.4)
		Median	4.0	3.9	10.3	14.7
	Impact (<i>n</i> = 17)	Mean (s.d)	7.0 (7.6)	12.9 (16.3)	26.5 (28.1)	37.6 (33.1)
		Median	3.5	6.8	14.7	25.5

⁷ Likely nutrient limitation determined from DIN:DRP ratios, based on the Redfield ratio of 16N : 1P (by atoms, equivalent to 7N : 1P by weight) observed in marine phytoplankton (Keck & Lepori 2012). As a general rule, ratios between say ~20 and ~5 (by weight) are inconclusive (Francouer et al. 1999). N : P > 20 usually indicates P limitation, and N : P < 5, N-limitation.

Broad patterns in % cover by filaments approximately reflect the pattern seen in DIN and DRP (i.e., increasing cover across the three categories of river site) (compare Table 6-1 with Table 6-3). However, correlation analyses show that relationships between mean % cover by filaments or the 92nd percentile of % cover by filaments (Table 6-3) and DIN or DRP are weak and non-significant, both across the whole dataset and within islands.

In contrast, % cover by mats was strongly and negatively correlated with DRP in the South Island (Spearman $R = -0.45$), but not in the North Island. The South Island pattern likely arises because of the negative association between didymo and DRP (Kilroy & Bothwell 2012).

These results reflect the great variability in percentage cover observations across sites, even using data averaged across 10 years. The assessment highlights the inherent difficulty in trying to link periphyton cover data with dissolved nutrient data on a site-by-site basis, even when other site characteristics are taken into account (Snelder et al. 2013). In that study, predictions of maximum cover at individual sites had large uncertainties (~80-100%). However, after aggregating sites by REC class, predictions of proportion of sites at which cover exceeded nominated criteria were relatively accurate (Snelder et al. 2014).

One interesting observation was that, in the North Island, water conductivity was more strongly correlated with % cover by filaments (Spearman $R = 0.36$) than with either DIN or DRP (Spearman $R = 0.06$ in both cases) (see Section 8.4.2). This pattern was not seen in the South Island, where the strongest correlate with % cover by filaments was DRP (Spearman $R = 0.20$).

7 Periphyton chlorophyll *a* and nutrient concentrations

Section 4.2 outlined potential difficulties in identifying relationships between periphyton and nutrient concentrations in rivers, because of interacting factors and sampling issues. To highlight these difficulties, literature was reviewed in two groups. The first group included studies in which periphyton and nutrient concentrations were measured at successive sites down river continua. The second group comprised studies of periphyton and nutrients at multiple sites across different rivers. Studies on seasonal patterns in periphyton – nutrient relationships were then considered, focusing on the relative importance of the two-way effects of nutrient concentrations on periphyton, and *vice versa*, at different times of year.

7.1 Longitudinal patterns

Downstream shifts in nutrient inputs, uptake and instream recycling can lead to corresponding shifts in the identity of the major nutrient (N or P) limiting periphyton growth, and therefore in periphyton abundance and community structure. Descriptions of such changes along rivers may therefore provide insights into the way nutrients influence periphyton growth and standing crop and *vice versa*. Longitudinal patterns in the biological and physical characteristics of rivers have been described in many studies, particularly in relation to the River Continuum Concept (RCC), first introduced almost four decades ago (Vannote et al. 1980). The RCC largely focussed on invertebrate community changes down river continua, and associated processing of detritus and primary production. Consequently, the number of studies located that specifically considered periphyton standing crop (measured as chlorophyll *a*) in relation to nutrient concentrations was lower than expected. In the following, studies in New Zealand are considered first, followed by selected studies (mainly from North America) focussing on gradients including agricultural and developed landscapes.

7.1.1 New Zealand studies

An important early study on the effect of nutrient enrichment in New Zealand rivers focussed on periphyton biomass upstream and downstream of point source discharges in the Canterbury and Manawatu regions (Welch et al. 1992). Up to four sites were sampled downstream of the discharges. The response of periphyton to measured DRP enrichment from the discharges was predicted from an existing model. Periphyton chlorophyll *a* was lower than predicted at many sites and this was attributed to invertebrate grazing. However, higher chlorophyll *a* was associated with higher DRP concentrations downstream of the discharges at all sites. At some sites, chlorophyll *a* was lower at sites farther downstream, corresponding to attenuation of the nutrient inputs.

Another early multi-site longitudinal investigation on periphyton in New Zealand was on the Motueka River (Biggs & Gerbeaux 1993). Over a downstream gradient of DIN from 35 to 170 mg m⁻³ and DRP of 2.0 to 5.7 mg m⁻³, mean chlorophyll *a* over one year was low (< 10 mg m⁻²) throughout the river, although maximum chlorophyll *a* of > 200 mg m⁻² was recorded at the two lower sites, compared with maxima of < 50 mg m⁻² at the two upstream sites. In another study in the Kakanui River, Otago (Biggs & Lowe 1994, Biggs et al. 1998) both DIN and DRP concentrations were relatively low throughout the river (<6 and <60 mg m⁻³, respectively). Mean periphyton chlorophyll *a* was low (< 20 mg m⁻²) and variable, and between-site differences were thought to be driven by habitat conditions and invertebrate grazing rather than by nutrient gradients.

The Pomahaka River catchment (Otago) extends from native tussocklands through low-intensity to high intensity farmland, including dairying. Strong gradients of increasing DIN and DRP accompanied the downstream land-use changes (summer 1996-7), along with downstream increases in periphyton

chlorophyll *a* (Harding et al. 1999). Maximum chlorophyll *a* exceeded 120 mg m⁻² at two of the three most downstream sites, corresponding to DIN and DRP up to 170 and 12 mg m⁻³, respectively (although no detailed concentration data were presented).

In a study of summer (January - March) periphyton accrual at four sites along ~40 km of the Hurunui River, Canterbury, nutrient-diffusing bioassays demonstrated that periphyton growth transitioned from N-limited at the most upstream site to P-limited at the most downstream site. DIN concentration increased by two orders of magnitude between the upstream and downstream site (<4 - > 400 mg m⁻³), but DRP was very low (< 2 mg m⁻³) throughout the river. Despite consistent P-limitation at the downstream site, periphyton on artificial substrata accrued to about 120 mg m⁻² over a 6-week period at that site and periphyton *in situ* on the riverbed exceeded 200 mg m⁻² on one survey date (Kilroy & Wech 2015). There was evidence supporting the proposal that the high periphyton standing crop at the downstream site could have been sustained by P sourced from fine sediment (Wood et al. 2015, and see Sections 4.3.2 and 8.1). There was almost complete turnover of community composition between the upstream and downstream site.

In a simultaneous study in a small tributary of the Hurunui River, periphyton chlorophyll *a* was relatively high in the headwaters (maximum of 57 mg m⁻²) compared to a site just upstream of the confluence (maximum of 30 mg m⁻²) and with the most upstream site in the Hurunui (<15 mg m⁻²). Correspondingly, mean DIN was higher in the headwater site than downstream (12.4 and 4.8 mg m⁻³ respectively), and taxa at the downstream site suggested N-limitation. DRP was higher at both sites than in the Hurunui mainstem (mean of 2.9 mg m⁻³). This pattern in the tributary suggested export of both N and P from the forested headwaters upstream of the sampling sites, but also net uptake of DIN between the two sites (NIWA unpublished data).

7.1.2 Overseas studies

Longitudinal studies overseas include situations that are uncommon or unknown in New Zealand, such as long rivers flowing from eutrophic reservoirs or nutrient-rich headwaters. Other examples describe scenarios more familiar to river managers in New Zealand.

One early study focussed on a stream affected by agricultural and other non-point-source nutrient inputs along its entire length (Lapwai Creek, Idaho, USA). Mean chlorophyll *a*, recorded in autumn, exceeded 150 mg m⁻² at all sites except the most upstream site and site 7 (of eight sites), and 200 mg m⁻² at three. However, DIN and DRP were relatively high at all sites. For example, in low flows, DIN and DRP at the most upstream and least impacted site were >1000 and >50 mg m⁻³ respectively, but this corresponded to low mean chlorophyll *a* (< 50 mg m⁻², Delong & Brusven 1992). The authors of this study emphasized that both nutrient concentrations and chlorophyll *a* were high in Lapwai Creek, compared to those in unimpacted streams in the same region. However, they offered no explanation for relatively low chlorophyll *a* at the upstream site, despite high nutrient concentrations.

In a two-year study in Carter Creek, Texas, Murdock et al. (2004) used artificial substrata to assess differences in periphyton accumulation at six sites. The stream gradient included wastewater treatment plants between sites 1 and 2 and 3 and 4. Highest periphyton accumulation was almost always recorded at site 2, and reached very high levels after only 6 days growth (>200 mg m⁻² on all four sampling occasions). This study illustrated extremely rapid periphyton development in nutrient concentrations apparently well above the levels thought to be associated with maximum uptake rates (see Table 6-1 and Section 6.4).

Along five sites spanning forest to agricultural / urban land use in the Appalachian Range, a 20-fold increase in mean chlorophyll *a* corresponded to a similar increase in NO₃-N and at least a doubling of DRP, with mean chlorophyll *a* exceeding 300 mg m⁻² at the two most downstream sites (Godwin et al. 2009). There was also a large increase in conductivity along the river. Similarly, mean chlorophyll *a* > 200 mg m⁻² was recorded only at the most downstream of three sites on Finkle Brook, New York State, in concentrations of 900 mg m⁻³ NO₃-N and 4.2 mg m⁻³ DRP. The most upstream site, with NO₃-N and DRP of 300 and 3.4 mg m⁻³ respectively had chlorophyll *a* < 50 mg m⁻² (Porter Goff et al. 2010).

Ten sites on the Ventura River were surveyed for periphyton cover, chlorophyll *a*, and nutrient concentrations on two occasions over summer (Klose et al. 2012). The filamentous alga *Cladophora* dominated cover at most sites in an early summer survey (June), and cover was varied in late summer (August). In both surveys, two reference sites in the upper catchment had low DIN and DRP (>50 and ~5 mg m⁻³ respectively) and chlorophyll *a* < 50 mg m⁻². DRP remained low until site 8, which was downstream of a wastewater treatment plant. However DIN was typically 500 - >1000 mg m⁻³ from site 3 downstream, and chlorophyll *a* was generally higher from this point (often > 200 mg m⁻²).

Relative to the purpose of the present review, the most interesting studies are those comparing chlorophyll *a* between periods before and after nutrient mitigation. One investigation was located which combined longitudinal data collection over two such time periods, along mainstem of the Clark Fork River, Montana, USA (Suplee et al. 2012). Municipal waste-water treatment plants in the upper reaches created gradients of declining TN and TP to the unimpacted lower reaches. Between 1998 and 2009, total phosphorus (TP) declined at five of the seven monitoring sites, but total nitrogen (TN) did not. Both periphyton biomass (as chlorophyll *a* and ash-free dry mass) and TP declined at three downstream sites. Periphyton biomass did not decline at two upstream sites despite a decline in TP. The authors concluded that TP concentrations needed to be lower than saturation levels to achieve the desired reductions in chlorophyll *a* (see Section 6.4).

The capacity of periphyton along a river continuum to adapt to changes in nutrient availability was illustrated by a study at nine sites downstream of a eutrophic reservoir in Oregon (Gillett et al. 2016). From the enriched reservoir outlet, NO₃-N and DRP concentrations declined along about 300 km of river from ~200 to ~ 50 mg m⁻³ (median NO₃-N) and ~120 to ~25 mg m⁻³ (median DRP). Several tributaries enter the river. Despite the large gradients, periphyton chlorophyll *a* declined only slightly in the middle of the river continuum, but was ~50 mg m⁻² at both the upstream and downstream sites. The biggest change was a downstream shift in community composition to dominance by diatoms capable of fixing nitrogen. The river described by Gillett et al. (2016) may be unlike any system in New Zealand, but the study illustrates how periphyton responds to changes in nutrient availability in ways that cannot be measured simply as chlorophyll *a*.

The results of these studies are summarised in Table 7-1. In general, periphyton chlorophyll *a* gradients along rivers corresponded to N and P gradients. This occurred regardless of the habitat sampled, and for both natural and artificial substrata (Table 7-1). Within rivers the effects of nutrient gradients should be clear, provided that habitat and substrate are kept consistent, and there are no major changes in hydrological patterns (e.g., from major tributaries). However, the absolute values of chlorophyll *a* linked to different N and P concentrations varied across rivers, and this is likely attributable to the different environments specific to each waterway and study design. Several other studies were located that examined the effects on river ecosystems of downstream gradients in nutrient concentrations, but did not include measurements of periphyton chlorophyll *a* (e.g., Dalu et al. 2015 focussed on algal community composition; Halliday et al. 2016 on dissolved oxygen).

Table 7-1: Summary of longitudinal studies discussed in Section 7.1. In all cases, periphyton biomass (as chlorophyll *a*) was measured at sites along a river continuum, along with nutrient concentrations. TN and TP were measured in some cases rather than DIN and DRP. The type of habitat sampled, and the sampling technique, are summarised where possible. In the Range columns, numbers in parentheses following the range indicate concentrations at the upstream and/or downstream sites, where they were not minimum or maximum. Numbers are approximate where they were estimated from graphed data.

Reference	River	No. sites	Dist. (km)	Sampling habitat and technique	Range, DIN (mg m ⁻³)	Range, DRP (mg m ⁻³)	Range, periphyton chlorophyll <i>a</i> (mg m ⁻²)	Comments
Welch et al. 1992	Seven rivers in Canterbury and Manawatu, NZ	Up to 5		Run habitat. Rock scrapings (n = 5 – 9).	23 - 4740	2 - 2690	4 - 1295	Upstream and downstream of point-source discharges. Increased chlorophyll <i>a</i> with nutrient enrichment was detected in all cases, though less than predicted in 5 of 7 rivers.
Biggs & Gerbeaux 1993	Motueka, NZ	5	-	Habitat not stated. Transect sampling rock scraping	35 to 170	2.0 to 5.7	<50 - >200 [peak values]	Means of 12 monthly surveys. General downstream increase in nutrients and chlorophyll <i>a</i> , peaking at site 4.
Biggs & Lowe 1994	Kakanui, NZ	5	-	Run habitat. Transects, rock scraping	14 - 56 (38)	<1 - 6	5 - 19 (lowest d/s)	Late summer survey; low nutrients throughout river.
Biggs et al. 1998	Kakanui, NZ	3	-	Run habitat. Transects, rock scraping	35, 22, 116	6,5,7	18, 14, 59	Heterogeneous habitat along river.
Harding et al. 1999	Pomahaka, NZ	15	119	Habitat not stated	10 - 180	4 - 12	<5 - ~90	Large jump in chlorophyll <i>a</i> between sites 11 and 12 (~75 km from top site); downstream lag between high biomass and high nutrients.
Kilroy & Wech 2015	Hurunui, NZ	4	~40	Run habitat, Rock scraping	5 - 374	0.6 - 1.1	11.6 - 123	Mean summer values. Invertebrate grazing controlled periphyton at site 3; didymo dominant at site 2. Co-limitation by N and P at site 1.
DeLong & Brusven 1992	Lapwai Creek, USA	8	48	Riffle habitat, artificial substrates	~1000 - ~2000 (500-1600)	200-500 - 70-80	>50 - >220	Eutrophic lake in upper catchment (upstream of site 2); nutrients and periphyton high from this point downstream
Murdock et al. 2004	Carter Creek, Texas, USA	6	~15	Artificial substrates, habitat not specified but water velocity measured	~1300 declining d/s	6400 declining d/s	<10 - > 500 after 6 days	Urban stream with point source inputs, artificial substrates, 6-day deployments.

Reference	River	No. sites	Dist. (km)	Sampling habitat and technique	Range, DIN (mg m ⁻³)	Range, DRP (mg m ⁻³)	Range, periphyton chlorophyll <i>a</i> (mg m ⁻²)	Comments
Godwin et al. 2009	Spring Creek, Pennsylvania, USA	5	-	Rock scrapings, no habitat information	200 - 4000	3.6 - 6.9	15.6 - 348	Mean values. Two-monthly sampling over one year, strong downstream increase in conductivity, separating sites 1 and 2 from 3 - 5.
Klose et al. 2012	Ventura, CA, USA	12	-	Visual. Water velocity measured	<50 - >1000 (~600)	~5 - >70	<40 - ~600	Visual assessments as well as chlorophyll <i>a</i> ; P-limitation upstream transitioning to N-limitation downstream. Mean values from two surveys.
Porter-Goff et al. 2010	Finkel Brook, NY, USA	3	-	Riffle habitat Rock scraping	300 - 900	3.4, 7.7, 4.2	<200 - >500 [peak]	Undeveloped to urban gradient
Suplee et al. 2012	Clark Fork River, Montana, USA (1998-2004)	7	383	100 m reach, up to 0.3 m depth. Filaments and other algae sampled separately	TN: 150 - 430	TP: 12 - 47 (30)	50 - 225 (178)	Declining nutrients in a downstream direction because of WWTPs in upper reaches; general correspondence between chlorophyll <i>a</i> and TN, TP
Suplee et al. 2012	Clark Fork River (2005-2009)	7	383	As above	TN: 150 - 350	TP: 11 - 32 (24)	24 - 275	Surveys following improvements to WWTPs (refer to text).
Gillett et al. 2016	Klamath River, OR, USA	8	306	Habitat not stated. Standardised depth and velocity. Rock scraping	200 - ~20	120 - <10	30 - 50 (lower in middle reaches)	Eutrophic lake upstream. Periphyton standing crop relatively constant despite downstream nutrient gradient, but community composition changed as DIN declined.

7.2 Between-river patterns

Insights into relationships between nutrient concentrations and periphyton chlorophyll *a* could potentially be gained using the results of surveys across multiple river sites and catchments. However, relationships between periphyton and nutrient concentrations are more likely to be obscured by the effects of other factors than in longitudinal studies, unless enough data are collected to allow an estimate of maximum standing crop (see Section 4.2).

A synoptic survey at 19 sites in four Otago streams combined longitudinal and between-river patterns (Niyogi et al. 2007a). Across all sites, benthic chlorophyll *a* was positively correlated with % catchment in pasture but was not correlated with either DIN (range of 7 to 1800 mg m⁻³) or TP. However, stream substrate type differed amongst streams and the results highlighted that stream-bed composition can be an important determinant of periphyton standing crop potential. In a separate synoptic study in Otago streams, epilithic chlorophyll *a* was positively correlated with nutrients (combined DIN and TP), although at the highest nutrient concentrations, the relationship flattened as fine sediment increased. Maximum DIN and DRP were ~1500 and >60 mg m⁻³ respectively, with maximum chlorophyll *a* of ~200 mg m⁻² (estimated from graph) at lower nutrient levels (Niyogi et al. 2007b).

A similar pattern in relation to stream-bed composition was observed in a comparison of Brazilian streams in neighbouring pristine and agricultural catchments. Despite tenfold higher DIN (7.6 vs. 62 mg m⁻³, respectively) and double the DRP (5.7 vs. 2.8 mg m⁻³ respectively) in agricultural streams, chlorophyll *a* did not differ between the pristine and agricultural streams. The agricultural streams were characterised by mid-stream shifting sediment. Periphyton biomass measured as total carbon (i.e. ash-free dry mass) was 7.5-fold higher in the pristine streams. However gross primary production was higher in the agricultural streams, and was also positively correlated with both DIN and NH₄-N concentrations. This study therefore again demonstrated how physical factors (low bed stability) had an overriding effect on periphyton standing crop, masking any effects of increased DIN and DRP (Gucker et al. 2008).

In another synoptic study at 41 stream sites in Southland, benthic periphyton chlorophyll *a* was not significantly related to instream DIN or DRP concentrations, or any combination of DIN or DRP and other environmental variables (including streambed substrate, water velocity, and land use) (Liess et al. 2012). Nutrient concentrations spanned wide gradients (29 – 1334, and 1 – 57 mg m⁻³ for DIN and DRP respectively) and were correlated with land use (% catchment in pasture). There were also significant negative relationships between the C:N and C:P ratios in periphyton and DIN and DRP respectively, indicating that periphyton in low nutrient streams contained relatively more carbon (such as extracellular mucilage) than high nutrient streams. This could reflect a shift in community composition across the nutrient gradient.

In common with two of the New Zealand studies mentioned above (Niyogi et al. 2007a, Liess et al. 2012), no strong relationships between peak chlorophyll *a* and any forms of N or P were detected across a set of 74 streams in Colorado, apart from a weak relationship with DIN (15% explained) (Lewis & McCutchan 2010). The ranges of concentrations covered was ~105 to 1200 mg m⁻³ for DIN and 0.4 to 195 mg m⁻³ for DRP.

In contrast, strong relationships between periphyton chlorophyll *a* and both TN and TP were found across 33 sites in 13 rivers in eastern Canada, even though each site was sampled once over three separate summers (Chetelat et al. 1999). Chlorophyll *a* of 9 – 470 mg m⁻², was measured across TN

and TP of 179 – 2873 and 6 – 130 mg m⁻³ respectively. Concentrations in the high range were well in excess of the saturating concentrations suggested by Dodds et al. (2006) (see Section 7.4). An interesting result in this study was that chlorophyll *a* was more strongly related to conductivity than to either TN or TP (see Section 7.4).

Scanlan et al. (2015) investigated relationships between mean chlorophyll *a* and TN and TP, collected over three seasons in 43 stream sites in Pennsylvania, USA. TN and TP ranges were 11 – 9330 and 10 – 1348 mg m⁻³ respectively. Significant correlations were identified between chlorophyll *a* (range 0.1 to 917 mg m⁻²) and TN. However, most emphasis was placed on the abundances of individual algal taxa and the strongest relationships were non-linear links to landuse, as percentage cover by forest.

The study by Biggs (2000a) took a different approach from the preceding examples. Biggs (2000a) used time-averaged data (monthly samples taken over at least one year) from 31 sites throughout New Zealand to identify relationships between mean and maximum chlorophyll *a* and mean DIN and DRP concentrations. Both nutrients were significantly related to chlorophyll *a*, but inclusion of a term to account for flood frequency (as “accrual period” the average number of days between flows exceeding three times the median flow) greatly improved the relationships. Over 70% of the variance in chlorophyll *a* was explained by relationships including days of accrual and either DIN or DRP. The predictive equations derived by Biggs (2000a) have been widely applied in New Zealand, although in the original paper it was stressed that regional relationships would likely provide more accurate relationships.

Subsequent to the Biggs (2000a) study, several regional councils have begun to accumulate datasets of periphyton over time, with the aim of developing regional relationships between periphyton, nutrient concentrations and flow. For example, in 2008 Horizons Regional Council initiated a programme of monthly monitoring of periphyton and a range of environmental variables at over 40 sites in the Manawatu – Whanganui Region (Kilroy et al. 2008). Preliminary analyses have indicated that even with detailed datasets and averaged data over up to three years, linking periphyton standing crop (as either chlorophyll *a* or percentage cover) is not straightforward (see Section 10.1 for further commentary).

In conclusion, as predicted (Section 4.2) synoptic surveys of multiple sites in different rivers and catchments rarely revealed strong relationships between periphyton standing crop (as chlorophyll *a*) and nutrient concentrations (the exception was Chetelat et al. 1999). In some cases, lack of relationships between periphyton and nutrient concentrations could be explained by other environmental differences between the sites. The single study in which time-series data were available (Biggs 2000a) identified positive correlations between maximum chlorophyll *a* and both DIN and DRP. Incorporating accrual period improved the relationships.

7.3 Seasonal periphyton - nutrient concentration relationships

The seasonal changes in rivers that have most effect on periphyton standing crop over time are related to flow conditions (see Section 7.1). However, given that some rivers experience regular and large seasonal fluctuations in nutrient (particularly DIN) concentrations (see Section 6.2), do these temporal changes in nutrient concentrations also affect periphyton standing crop through altering growth rates when flow conditions favour biomass accrual?

The relationship between periphyton and nutrients can also be viewed from the alternative perspective of the effect of periphyton on DIN and DRP concentrations. Many of the studies discussed in Section 5 concluded that uptake by primary producers accounted for most of the

measured nutrient removal in streams. Consequently, although excessive periphyton is often viewed as undesirable, these growths may also be viewed as an “ecosystem service” because of their ability to reduce concentrations of DIN and DRP (Dodds 2003, Niyogi et al. 2004, Hill et al. 2010), and subsequent export of nutrients to sensitive downstream receiving waters such as estuaries (Schiel & Howard-Williams 2016) (see Section 7.3.2). Under what conditions is periphyton capable of reducing nutrient concentrations enough to mitigate additional inputs to a stream?

7.3.1 Effects of seasonal nutrient fluctuations on periphyton

The short-term effects of DIN and DRP additions in increasing periphyton growth rates, leading to higher standing crop (assuming that at least one of the nutrients has background concentrations that limit growth), have been demonstrated in many experiments (Larned 2010). Identifying such short-term effects on periphyton standing crop in rivers is more difficult, mainly because of the confounding effects of other environmental factors, particularly flows (Biggs 1995). In addition, the short-term effects of nutrient uptake by periphyton on nutrient concentrations could prevent identification of responses by periphyton standing crop to nutrients at the same time scale. However, in many situations, it may be theoretically possible to link periphyton accrual rates to ambient nutrient concentrations as they change over time because periphyton (and other processes) will usually be removing N or P from the water column at rates much lower than the influx of nutrients from upstream (see Section 7.3.2).

In New Zealand rivers, peaks in nutrient concentrations generally occur in winter (July – August), and the winter maxima often coincide with elevated flows (see Section 4.6.2). Therefore, the effects of high flows in reducing periphyton standing crop (through scouring) are likely to offset any stimulatory effects on periphyton of maximum nutrient concentrations in winter. Nevertheless, it is possible that increasing concentrations in late summer to autumn might stimulate periphyton, creating autumn peaks in standing crop. For example, a recent analysis of seasonal patterns of chlorophyll *a* and periphyton cover in the Manawatu-Wanganui region at up to 62 sites showed that almost half the occurrences of annual chlorophyll *a* maxima occurred in the quarter April to June (Kilroy et al. 2016).

The effect of seasonal fluctuations in DIN may be evident in the Upper Ohau River, Canterbury, for a particular algal species. The Upper Ohau drains Lake Ohau and has a consistent, controlled flow of 10-12 m³ s⁻¹. The periphyton is dominated by the introduced diatom, *didymo*. In surveys in 2016, more than 3 years following the most recent major flood, we recorded over twice as much chlorophyll *a* in July than in March (respectively, 217 ± 119 vs. 86 ± 57 mg m⁻²). This biomass corresponded to mean DIN concentrations of 14 mg m⁻³ in July and 2.2 mg m⁻³ in March. DRP did not differ between surveys (NIWA unpublished data). Previous experiments in the Upper Ohau showed that *didymo* growth was N-limited below concentrations of about 10 mg m⁻³ (Kilroy & Larned 2016), and the results of the survey were consistent with that finding. These DIN concentrations are lower than those likely to be encountered in stream in an agricultural landscape, but the results illustrated that a small increase in DIN appeared to have a large impact on chlorophyll *a* (assuming that no other environmental factor was responsible for low chlorophyll *a* in March).

Overall, long datasets (e.g., at least 6 years) of linked periphyton standing crop data, with associated nutrient concentrations are likely to be required to establish the significance of seasonal differences in nutrient supply in relation to meeting the requirements of the NPS-FM (see footnote, Section 3.3). In most rivers, the effects of variability in flows will obscure the effects of nutrients in stimulating growth over short time-scales.

7.3.2 Effect of periphyton on nutrient concentrations

The effect of high concentrations of planktonic green algae on N concentrations has been well-studied in investigations on high-rate algal ponds (HRAPs), which are designed to remove nutrients from municipal effluents prior to discharge (Sutherland et al. 2015). As an example, in such a system, $\text{NH}_4\text{-N}$ concentrations of 48000 mg m^{-3} stimulated growth of the green alga *Chlorella vulgaris*, which assimilated most of the N (Alcantara et al. 2015).

Periphytic algae are unlikely to have the same potential for nutrient removal as planktonic algae, because the surface area for uptake is limited to the stream bed. However, summer low flows along with reduced or no catchment runoff can result in nutrient-stripping in some rivers. In addition, research is currently underway on the design of structures that optimise periphyton growth (particularly filamentous algae) for the purpose of nutrient removal in flowing waters (filamentous algae nutrient scrubbers or FANS; see Sutherland & Craggs 2016 for a review).

The potential effect of nutrient removal (through uptake by periphyton, and through other processes such as denitrification) can be estimated for any river by comparing the amount of uptake in an area of stream bed over a given time with the amount of nutrient passing over that area in the same time. Using literature estimates of areal uptake rates (U) under appropriate conditions, estimates of water depth, volumetric flow and ambient DIN or DRP concentration at the site of interest, and assuming a constant depth across a reach, the proportion of nutrient removed by periphyton is:

$$(U * A) / (C_{\text{nutrient}} * Q) \quad \text{or} \quad U / (C_{\text{nutrient}} * D)$$

Where U is the published uptake rate ($\mu\text{g m}^{-2} \text{ s}^{-1}$), A is area of riverbed covered in 1 second (m^2 , calculated from volumetric flow Q ($\text{m}^3 \text{ s}^{-1}$) divided by water depth D (m), and C_{nutrient} is the nutrient concentration ($\mu\text{g m}^{-3}$).

Simon et al. (2005) summarised published uptake rates from multiple studies and reported maximum uptake rates ($\mu\text{g m}^{-2} \text{ s}^{-1}$) of 10.4, 8.1 and 1.9 for NH_4^- , NO_3^- and PO_4^{3-} , respectively. To extend the above calculation to long reaches, the cumulative effect of concentration reductions in successive reach sections would need to be estimated. However, within a single reach, it can be shown that instream uptake starts to reduce concentrations appreciably (e.g., > 5% reduction) only in very shallow water depths (< 0.2 m) and when the starting concentrations of N or P are also very low (e.g., < 20 mg m^{-3}).

At high ambient nutrient concentrations (e.g., > 300 mg m^{-3}), biotic uptake rates may be offset by increasing rates of re-mineralization and declining denitrification (Dodds et al. 2002, Mulholland et al. 2008) (see Section 10.1). For DIN in particular, net uptake rates will decline, leading to downstream export of most nutrient molecules.

In summary, uptake of nutrients by stream periphyton always affects ambient concentrations to some extent, but the effect is generally negligible except in very long periods (generally in summer) of declining water depth over long, shallow, stream reaches with no tributary inputs that introduce nutrients, and when starting concentrations are low. It may be possible to design systems (filamentous algae nutrient scrubbers) that improve of the natural capacity of periphyton to remove nutrients, and these are currently being researched.

7.4 Saturating concentrations of DIN and DRP

The nutrient concentrations above which periphyton standing crop no longer increases (i.e., nutrient saturation is reached) are important because remediation of the effects of nutrients on periphyton standing crop are theoretically possible only at concentrations below saturation (Suplee et al. 2012).

7.4.1 DIN

Saturating concentrations of DIN probably vary across rivers and regions. One reason for the variation is that other unknown factors may limit periphyton growth rates and standing crop. In Michigan streams Hoellein et al. (2007) observed saturation of $\text{NO}_3\text{-N}$ uptake (from all sources, including periphyton) at about 760 mg m^{-3} , while no saturation was seen in $\text{NO}_3\text{-N}$ concentrations up to 700 mg m^{-3} in a Kansas stream (Dodds et al. 2002). In a southeast Michigan stream Bernot et al. (2006) reported saturation at $\sim 400 \text{ mg m}^{-3}$. In experiments in New Zealand, net uptake of $\text{NO}_3\text{-N}$ was observed to saturate in concentrations of $310 - 370 \text{ mg m}^{-3}$, in spring, in high light conditions (Matheson et al. 2012). Uptake rates of $\text{NO}_3\text{-N}$ across six Otago streams were correlated with $\text{NO}_3\text{-N}$ concentration and DRP concentration (marginally) in both winter and summer, but this measure of uptake was not related to periphyton chlorophyll *a* (Niyogi et al. 2004). No saturation of uptake was observed across the range of $\text{NO}_3\text{-N}$ measured (up to 264 mg m^{-3}).

DIN concentrations that are saturating for uptake may not correspond to those associated with maximum periphyton growth rates, or with maximum standing crop (as chlorophyll *a*) because uptake measures typically include uptake (or removal from the overlying water) by all processes. There may also be differences between concentrations that saturate periphyton growth rates and those associated with maximum standing crop because algae may continue to accumulate when DIN saturates growth rates only at the surface of the mat.

Using a large dataset, Dodds et al. (2006) suggested saturation points for TN and TP corresponding to breakpoints in the relationship between $\log(\text{maximum chlorophyll } a)$ and $\log \text{ TN}$ or $\log \text{ TP}$, of 367 and 27 mg m^{-3} . Maximum chlorophyll *a* at the suggested saturation point for TN was, on average, $\sim 150 \text{ mg m}^{-2}$. The underlying regression relationship had low explanatory power (R^2 of 0.24), therefore we assume that the range of values was high (not illustrated in Dodds et al. 2006).

In New Zealand periphyton – nitrogen relationships have been explored and developed mainly using DIN rather than TN. However, TN and DIN are often closely correlated. For example in the NRWQN dataset (see Section 5), DIN and TN are related with the linear regression equation:

$$\text{DIN} = -84.43 * 0.869 \text{ TN} \quad (n = 77, R^2 = 0.952)$$

From this equation, the Dodds et al. (2006) TN concentration at which periphyton chlorophyll *a* tends to stabilise (i.e., the saturation point), on average, corresponds to DIN of 234 mg m^{-3} .

In a meta-analysis of nutrient limitation experiments with periphyton responses measured as the ratio of chlorophyll *a* in enriched versus control treatments, an upper saturation concentration for DIN of about 1400 mg m^{-3} was suggested, although responses to increases in DIN started to level off above about 280 mg m^{-3} (Keck & Lepori 2012). Keck & Lepori (2012) did not distinguish between lack of effect attributable to P-limitation or limitation by some other factor. However, correspondence of their suggested saturation concentration range with that of Dodds et al. (2006) may indicate that some of the observations of no effect could be attributed to DIN saturation.

7.4.2 DRP

Excessive chlorophyll *a* (e.g. > 200 mg m⁻²) has been reported when DRP exceeds at about 10 mg m⁻³ (e.g., Bothwell 1989). In experiments, a PO₄³⁻ concentration of approximately 28 mg P m⁻³ was shown to correspond to peak chlorophyll *a* of approximately 350 mg m⁻² (Bothwell 1989). In an analysis of a large dataset of nutrient limitation experiments, a flattening off (or breakpoint) in the TP versus chlorophyll *a* response relationship occurred at TP between 30 and 60 mg m⁻³, but the breakpoint for DRP was unclear (Keck & Lepori 2012).

The explanation for the wide range of potentially saturating concentrations (10 – 60 mg m⁻³) may be that dense accumulations of periphyton require higher P concentrations to maintain growth in the whole mat than the very low concentrations required to maximise cell division rates at the mat surface (Bothwell 1989). DRP release from particulate P within in the mat could also contribute to the variability (see Sections 4.3.2 and 8.1). DRP requirements also differ across algal groups. For example, Bothwell (1988) observed that cellular growth rates in a diatom-dominated biofilm appeared to saturate at DRP concentrations of 0.3 – 0.6 mg m⁻³; however growth rates larger green filamentous algae such as *Stigeoclonium* sp. and *Cladophora* sp. saturate at DRP concentrations > 25 mg m⁻³ (Bothwell 1989).

The saturation point suggested by Dodds et al. (2006) for TP was 27 mg m⁻³, based on a USA-wide dataset. This value for TP corresponded to average maximum chlorophyll *a* of ~100 mg m⁻², although with high variability (R² = 0.11). Dodds et al (2002) noted that potentially N-limited periphyton (TN : TP < 15) tended to have lower chlorophyll *a* for any given TP values than periphyton in streams with TN : TP > 15). Note that DRP and TP are not strongly correlated in the NRWQN dataset and a corresponding value for DRP could not be derived in the same way as for DIN.

While the Dodds et al. (2002) average saturation point for TP is close to the Bothwell (1989) value for DRP, Smucker et al. (2013) proposed a much higher saturation threshold (TP of 82 mg m⁻³) above which periphyton community composition and biomass were not expected to change further (using data from 87 streams in Connecticut, USA). The discrepancy between Dodds et al. (2006) and Smucker et al. (2013) could indicate that there are regional differences in saturation points. A recent study provided support for regional patterns: streams in two physiographically separate provinces in Pennsylvania, USA, displayed different responses to P-enrichment, which may have been linked to “the [different] interactive effect[s] of base chemistry and land use on the physiology of biofilms in these ecosystems” (Price & Carrick 2016). This implies that similar variability in saturation points may exist between geologically distinct regions in New Zealand.

7.5 Chlorophyll *a*, DIN and DRP: synthesis

From Section 7.4, estimates of DIN values above which **uptake** is saturated ranged from ~250 to >750 mg m⁻³. Estimates of DIN concentrations above which periphyton **standing crop** accrual slows markedly were more consistent, at 230 – 280 mg m⁻³. Corresponding values for DRP were unclear, but for TP ranged from 10 to >80 mg m⁻³. An experimentally derived saturating concentration for DRP of ~28 mg m⁻³ (applicable to periphyton standing crop) corresponds well with the DIN threshold range for standing crop because the N : P ratio is close to the theoretical cellular ratio for algae (the Redfield ratio, see footnote, Section 5.3). Maximum chlorophyll *a* corresponding to the suggested saturating concentrations appears to be variable, ranging from (on average) ~100 to ~350 mg m⁻². Results from different regions in the USA indicate that there may be regional variation (e.g. linked to physiographical differences) in responses to P-enrichment. Given the heterogeneous geological and hydrological landscape of New Zealand, regional variability in responses may be expected here.

In the longitudinal studies reviewed (see Section 7.1 and Table 7-1), the chlorophyll *a* threshold defining the bottom line in the NPS-FM (200 mg m⁻², see footnote, Section 3.3) was exceeded at DIN values ranging from 170 to 4000 mg m⁻³ and DRP from 5.7 to > 70 mg m⁻³. The maximum chlorophyll *a* value reported was 600 mg m⁻², in 600 and >70 mg m⁻³ DIN and DRP, respectively (Klose et al. 2012). The data available included single values from surveys carried out over a short time period, or means or ranges from repeat surveys. In some cases the data were presented graphically and the numbers are estimates. Overall it was difficult to extract useful quantitative data. However almost all the surveys showed responses by chlorophyll *a* to nutrient gradients along rivers, regardless of the habitat sampled or the sampling technique. In single rivers, consistency of sampling is likely to be more critical than the techniques employed. In the one study carried out over a long period (on the Clark Fork River), Suplee et al. (2012) showed how management-led reduction of TP to the river resulted in chlorophyll *a* reductions at sites where concentrations fell below presumed saturating concentrations of TP.

The surveys of chlorophyll *a* and nutrients between rivers showed few strong patterns (Section 6.2). Unless surveys incorporate time-averaging of data, clear relationships with any measure of standing crop are unlikely because river-specific, site-specific and time-specific factors all combine to influence standing crop at any one time. The study of 31 New Zealand rivers (Biggs 2000a) was the only example located which included time-series data. This study successfully demonstrated relationships between chlorophyll *a* and DIN or DRP, particularly if accrual time was accounted for. Synoptic surveys are more likely to reveal relationships between nutrient concentrations and other measures of algal growth and productivity (e.g., Giling et al. 2013). Within-river relationships over time are equally difficult to identify except in situations of prolonged stable flows or very long time series (e.g., Suplee et al. 2012) (Section 7.3).

Little information was located on the effects of seasonal changes in nutrient concentrations on periphyton standing crop (as chlorophyll *a*), probably because in these seasonal changes coincide with flow changes, which have an overriding effect on periphyton standing crop. The potential effect of periphyton standing crop on removal of nutrients from the water column was evaluated. The conclusion was that removal rates are generally negligible except in long periods of declining water depth over long, shallow, stream reaches, when starting concentrations are low.

8 Interactions between nutrients and other factors influencing periphyton abundance and community composition

8.1 Effect of flow variability and geomorphology

In most rivers, a critical determinant of periphyton standing crop at any given time is preceding flow conditions, particularly the time elapsed since the most recent bed-clearing flood (Biggs 1995, 2000a). The effect of the interaction between flood frequency and nutrient concentrations on broad-scale patterns of maximum periphyton standing crop were demonstrated in the survey-based analysis by Biggs (2000a) (see Section 6.2). At the scale of algal cells, the variation of water velocity that accompanies changes in flow can have two opposing effects. Up to a certain point, increasing water velocity enhances delivery of nutrients to cells, and stimulates growth (Larned et al. 2004) (see Section 4.4.3). Beyond some critical point, drag forces start to remove periphyton (Biggs et al. 1999).

Periphyton removal in high flows becomes more effective once the river bed sediment bed starts to move. An experimental study showed that sand abrasion enhanced the effectiveness of periphyton removal (Francoeur & Biggs 2006). The important role of abrasion by moving sand in periphyton removal has recently been confirmed in a field study (Hoyle et al. in press). Important findings by Hoyle et al. (in press) were that (a) the frequency of mobility of fine bed-material (sand) appeared to be the dominant control on periphyton standing crop; and (b) nutrient concentrations had been positively correlated with periphyton chlorophyll *a* at sites where the frequency of sand movement was low, but not at sites where sand moved frequently.

At a smaller scale, the physical properties of the rock itself could potentially affect periphyton growth. The chemical composition of a wide range of rock types (including pumice, schist, greywacke, limestone) does not appear to affect periphyton accrual rates, at least in short-term experiments (Bergey 2008). However, the surface texture of rocks has been shown to have a significant effect on periphyton accrual, with rougher surfaces accumulating more periphyton than smoother surfaces in otherwise identical growth conditions and sampling with a brush technique (Murdock & Dodds 2007). These authors also demonstrated that an increasing proportion of chlorophyll *a* was left behind on the surfaces after brushing (commonly used for sampling in New Zealand, Kilroy et al. 2013) as roughness increased. The implication for interactions with nutrients is that periphyton growing on rough rock types is likely to respond faster to increases in concentrations of a limiting nutrient than that on smoother rock.

In conclusion, river flow, combined with the geomorphological characteristics of a river site, may interact with nutrients over a range of scales in either reducing or enhancing the potential for development of high periphyton standing crop. In theory, periphyton at geomorphologically stable sites with infrequent bed movement and rough-textured rock should be most responsive to increases in nutrients; and sites with mobile sediments of smooth rock types should be least responsive. Thus, physical and geological characteristics of a site may contribute to defining the potential response to nutrient enrichment (see also Section 7.4.2).

8.2 Effect of light (shading)

Limitation of periphyton growth and standing crop in shaded streams is well documented (Hill et al. 1995, Hill 1996, Larned 2010). Consequently, shading of small streams has often been suggested as a means of improving stream ecosystem health by reducing excessive periphyton growth (Sturt et al. 2010, Burrell et al. 2014, Halliday et al. 2016). In relation to nutrients, Von Schiller et al. (2007) found

in nutrient-diffusing substrate experiments that light had more effect on periphyton than nutrient additions. Background DIN and DRP concentrations were 134 – 791 and 14 – 38 mg m⁻³, respectively.

Algae can adapt to low-light conditions. In a two year experiment, periphyton chlorophyll *a* responded positively to nutrient additions despite heavy shade (up to 200 μmol photon m⁻² s⁻¹ in summer)⁸ (Veraart et al. 2008); in this study, gradual shifts in taxonomic composition, with higher densities of larger-sized taxa in enriched conditions, suggested that periphyton was capable of adapting to low light in the longer term. Even so, maximum chlorophyll *a* was less than 120 mg m⁻² in DIN and DRP concentrations of 760 and 30 mg m⁻³ respectively. Experiments in stream-side channels at Whatawhata, Waikato, similarly demonstrated adaptation of periphyton photosynthetic rates to low light (<100 μmol photon m⁻² s⁻¹, or >90% shade), although highest chlorophyll *a* was observed at 60% and 0% shade (Quinn et al. 1997). In a survey of North Island streams, periphyton standing crop exceeding 100 mg m⁻² only occurred at sites where the incident light was >3% of unobstructed sky light (Davies-Colley & Quinn 1998). Incident light of less than 3% required heavy shading by tall trees, and such complete shading occurred only at stream sites where the waterway width was less than 4.5 to 5.5 metres (depending on tree height).

While the effect of shading is generally to reduce periphyton standing crop, there are potential consequences for nutrient uptake. For example, increased export of organic nitrogen has been linked to reduction of shading effects as river size increased (Finlay et al. 2011). Overall, the effect of light in mitigating the effects of eutrophication (Burrell et al. 2014) needs to be balanced by the potential for streamside planting to lead to increased nutrient export to downstream reaches (McKergow et al. 2016; and see Sections 9.3, 10.2).

8.3 Effect of invertebrate grazing

Many invertebrate taxa depend on benthic algae as a food source. Consequently, if grazing invertebrates are present in a stream, they must be reducing algal biomass to some extent. Biomass reductions were reported in over 75% of studies on responses of periphyton to grazers (Steinman 1996). The effect of grazers on periphyton is variable and depends on both the identities of the grazers present and their densities and the identities and growth forms of the algal taxa in the periphyton (Peterson et al. 2001). Ultimately both of these factors depend on the physico-chemical character of the stream or river, including temporal variability. The conditions under which grazing rates are maximised are of interest in terms of complying with the NPS-FM (see footnote 3, Section 3.3).

High rates of grazing also increase nutrient cycling rates in streams, through ingestion of algae followed by excretion of soluble nutrients, which are then available for further periphyton growth (Vanni 2002). The consequences for primary production may be determined by the magnitude of the imbalance between N:P ratios in periphyton and invertebrates. Invertebrates tend to require higher proportions of N than algae. Therefore grazing could exacerbate P-limitation if background levels of bioavailable P are low enough (Bowman et al. 2005). In addition to being recycled within the system nutrients could also be translocated from the system (e.g., through insect emergence) (Vanni 2002).

A range of studies has confirmed great variability in interactions between algal standing crop, nutrients and grazing effects. Lamberti et al. (1989) determined experimentally that grazing increased primary production rates slightly, through rapid growth rates in algae as the periphyton layer was grazed, but this effect was only evident at low or moderate light levels. In laboratory

⁸ Typical light measurements in full sun range from 1500 to >2000 μmol photon m⁻² s⁻¹

experiments with two types of caddis fly grazers, Anderson et al. (1999) showed that grazing of periphyton outstripped the stimulatory effect of increasing DIN and DRP to concentrations exceeding or close to suggested saturating concentrations (see Section 7.4). Anderson et al. (1999) suggested that, under the conditions of their study, invertebrate dry mass of $>1500 \text{ mg m}^{-2}$ would prevent periphyton from attaining a “nuisance level”, defined as chlorophyll *a* $>150 \text{ mg m}^{-2}$. In a reach-scale experiment using pulsed electric shock exclusion of invertebrates, Taylor et al. (2002) reported a $>50\%$ increase in chlorophyll *a* following reduction of invertebrates (mainly Ephemeroptera, which graze on periphyton). Ambient nutrient concentrations in the treatment reach were relatively low (DIN and DRP of ~ 20 and 4 mg/m^3 respectively) and chlorophyll *a* increased from <10 to $>20 \text{ mg/m}^2$ following removal of grazers.

A review of indirect effects of invertebrate grazing on periphyton (such as “habitat facilitation”, which includes alteration of nutrient cycling) concluded that the overall relationship between grazer density and productivity by area was negative, but productivity by biomass (of periphyton) increased (Liess & Hillebrand 2004). Thus grazers both reduced standing crop and increased growth rates and nutrient incorporation in the remaining algae (e.g., Hillebrand et al. 2002). This conclusion was reached in an analysis of results from many experiments. Nevertheless, in a survey of 74 Colorado streams, there was a positive relationship between chlorophyll *a* and both total invertebrate abundance and the abundances of most grazing taxa (Lewis & McCutchan 2010), suggesting simultaneous increases in both food supply and consumers across streams.

The potential for invertebrates to reduce periphyton standing crop has been shown to strongly depend on preceding flow conditions. Periphyton accrual can be rapid following high flows that deplete populations of grazing invertebrates (Biggs & Stockseth 1995, Rutherford et al. 2000). Very large floods can have prolonged negative effects on both trophic levels (Robinson et al. 2004). On the other hand, frequent small-sized flood disturbances may promote the effectiveness of grazer control of periphyton by maintaining a periphyton community comprising edible taxa, rather than late stage filamentous algae that are less edible (Murdock et al 2004). A similar effect of frequent floods was demonstrated using flow and sediment supply manipulations in a full-scale experimental stream (Merten et al. 2010). In treatments subject to high bedload abrasion, which reduced chlorophyll *a*, the presence of grazers led to even lower chlorophyll *a* compared to treatments with no grazers. In addition, grazers had a stronger effect on chlorophyll *a* as water velocity increased up to a maximum of 0.55 m s^{-1} , compared to ungrazed treatments.

Any seasonal patterns in invertebrate grazing potential in New Zealand streams are most likely to be driven by seasonal flow patterns. Seasonal ontogenetic shifts in macroinvertebrate populations can be important in some regions, but life histories of stream macroinvertebrates in New Zealand are generally “seasonally flexible” (Hart 1985).

Several studies have directly investigated the interactive effect of invertebrate grazing and other controls on periphyton, using electrical exclusion plots (as used by Taylor et al. 2002 – see above) in natural stream habitats. Sturt et al. (2011) assessed the effects of nutrients, light and grazing on periphyton by carrying out their experiment upstream and downstream of a waste-water treatment plant outfall, with DIN and DRP up to 8000 and 50 mg m^{-3} , respectively. In all cases heavy shade strongly reduced periphyton chlorophyll *a*, with or without grazers. In unshaded treatments, excluding grazers led to increased cover by the green alga *Cladophora* and increased chlorophyll *a* by up to 60-fold. The conclusion was that “... despite high nutrient loadings, even those associated with sewage-related inputs, grazing invertebrates were able to control the majority of nuisance algal growths” (Sturt et al. 2011). The nutrient enrichment itself may have stimulated the development of

large grazer populations, and this effect may be especially pronounced below WWTPs through changes to nutrient content of algae that improve their food value (Bowman et al. 2005, Singer & Battin 2007). The extremely heavy grazing reported by Sturt et al. (2011) appears to be unusual.

In another grazer exclusion experiment, Lourenco-Amorim et al. (2014) directly tested for the interactions between grazing pressure and nutrient effects on periphyton using nutrient-diffusing substrata as nutrient sources, in much lower ambient nutrient concentrations (DIN and DRP of ~ 130 and ~ 7 mg m⁻³ respectively). After 15 days, periphyton chlorophyll *a* showed a strong response to nutrient addition alone; grazers alone reduced chlorophyll *a* by a small amount; and the combination of grazers and nutrient addition resulted in a very small increase in chlorophyll *a*.

Interactions between grazer effects and the stimulatory effect of water velocity on periphyton nutrient uptake (Larned et al. 2004) and standing crop (Townsend et al. 2012) have also been demonstrated experimentally. Hintz & Wellnitz (2013) showed that grazer removal of chlorophyll *a* at higher water velocities (up to 0.4 m/s) more than compensated for the higher chlorophyll *a* accumulation under those velocity conditions (as demonstrated by higher chlorophyll *a* in the control treatments with no invertebrates). Merten et al. (2010) reported a similar response to water velocity (see above). No experiments were located which tested the effects on periphyton standing crop of nutrient additions, current velocity and grazer effects at the same time. Such experiments may be informative (e.g., Greathouse et al. 2006) in terms of identifying conditions under which the effects of grazers may assist in limiting periphyton chlorophyll *a* to avoid D-Band of the NPS-FM periphyton attribute (see footnote 3 in Section 3.3).

The interaction between grazing invertebrates and periphyton may also be influenced by the presence of predators. Biggs et al. (2000) found that streams with populations of trout (which predate on invertebrates) had higher periphyton chlorophyll *a* than streams without trout. The implication was that periphyton development was being curtailed by invertebrate grazing in the non-trout stream. Periphyton in both types of stream responded positively (i.e., increased chlorophyll *a*) to short-term nutrient enrichment.

A recent local example of heavy invertebrate grazing apparently limiting periphyton accrual was seen in one of four river sites surveyed in the Hurunui River, Canterbury, during a period of low flows in January-February 2015 (Kilroy & Wech 2015). Periphyton accrual rates were lowest at a site with mean DIN and DRP of 46 and 0.7 mg m⁻³ respectively and where invertebrate activity was visible (e.g., as grazers on tiles deployed to measure accrual rates). The reasons for such active grazing were unclear. Our measurements of water velocity and substrate composition did not indicate substantial differences from the other sites. Following floods later in the season, periphyton chlorophyll *a* at this site accrued to levels similar to that at other sites where nitrogen was not limiting (~ 70 mg m⁻²) over a period of 42 days (Kilroy & Wech 2015).

Overall, grazing macroinvertebrates can have a strong effect on periphyton standing crop in many situations. Therefore, creating good stream habitat for invertebrates could contribute to reducing chlorophyll *a*. Favourable conditions for invertebrate grazing were identified by Greenwood et al. (2012) and Burdon et al. (2013). These include faster water velocities and low (< 20%) levels of fine sediment. Responses to stream habitat changes by invertebrates (as both density and community composition) has been reviewed elsewhere (e.g., Winterbourn 2004). The presence of predators (e.g., trout) may influence grazing intensity and counteract beneficial grazing effects on periphyton, accentuating nuisance algal risks.

8.4 Effect of water chemistry

Nitrogen and phosphorus are generally assumed to be the nutrients most likely to limit periphyton growth in freshwaters, and the literature is dominated by studies on the effects on periphyton of changes in levels of these major nutrients (but see Gomez-Consarnau & Sanudo-Wilhelmy 2015). The algae in periphyton also have absolute requirements for other nutrients, including iron (Fe), molybdenum (Mo) and cobalt (Co). The role of iron as a potentially limiting nutrient in freshwaters has received some attention (Larson et al. 2015). Larson et al. (2015) concluded that iron limitation of periphyton in rivers could be more widespread than currently thought. A review of existing data on iron concentrations may help to identify if iron limitation could influence periphyton in New Zealand rivers.

In general micronutrients are rarely considered in freshwaters, although soils in some parts of New Zealand have deficiencies in, for example, Mo and Co, which are remedied through supplements in fertilizers. A recent study identified micronutrient limitation of phytoplankton in a eutrophic lake, highlighting that the trace elements tested (Fe, boron (B), copper (Cu), Mo and Co) may be more important than generally believed in driving lake phytoplankton composition and biomass (Downs et al. 2008). However, there appear to be no reports of any effects on periphyton in streams.

Agricultural practices may lead to increasing concentrations of cations into surface waters, such as potassium (K) from fertilisers. Potassium additions are unlikely to have any effect on periphyton because concentrations typical in surface water are not thought to be growth limiting, and levels at which K is toxic to algae are very high (Talling 2010).

Measures of conductivity (also known as electrical conductivity, EC) are commonly used to represent the sum of major dissolved cations (calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), and K^+) in water. Cation composition (and therefore conductivity) is mostly a function of the geological setting of a catchment rather than catchment activities. However, changes in nutrient concentrations along a river continuum, or over time, can be detectable as changes in conductivity (Likens et al. 1970, Kim & Furumai 2013, Ballantine & Davies-Colley 2014). In the USA, conductivity is routinely measured in citizen science programmes, and methods have been developed to distinguish sites with natural conductivity from those where conductivity is influenced by catchment activities (Kney & Brandes 2007, Thomson et al. 2012). Conductivity is used as an indicator of stream health (Thomson et al. 2012), presumably based on the positive relationship between conductivity and alkalinity (i.e., acid-neutralising capacity). Increasing alkalinity influences the efficiency of carbon fixation and primary productivity of aquatic ecosystems (Dodds 2002).

The positive relationship between conductivity and productivity was confirmed in one of the earliest wide ranging surveys of periphyton in New Zealand. Water conductivity emerged as the variable associated most strongly with periphyton community composition and biomass (measured as ash-free dry mass) across >400 sites (Biggs & Price 1987). This finding was replicated in a subsequent survey at different sites (Biggs 1990). In a synoptic survey in 25 rivers in eastern Canada, Chetelat et al. (1999) reported that water conductivity (range: 65 – 723 $\mu\text{S cm}^{-1}$) explained 71% of the variance in periphyton chlorophyll *a* (range: 9 – 470 mg m^{-2}). The explanatory power of conductivity exceeded that of all other environmental variables considered (including N and P). Communities with high chlorophyll *a* in both the New Zealand and Canadian studies were dominated by the filamentous green alga *Cladophora*. Chetelat et al. (1999) suggested that the positive relationship between *Cladophora* abundance and conductivity could be driven by a requirement for Ca^{2+} by this taxon.

In a regression tree analysis of chlorophyll *a* in relation to environmental data (including N and P) from 89 stream sites in eastern USA, conductivity was the primary factor separating sites with high and low chlorophyll *a* (Pan et al. 1999). The threshold separating the two groups was 226 $\mu\text{S cm}^{-1}$. Numerous other studies have demonstrated links between conductivity and periphyton community composition (e.g., Potapova & Charles 2003, Rott & Schneider 2014).

Conductivity was also one of the strongest predictors of chlorophyll *a* in recent analyses of periphyton data from New Zealand rivers (e.g., in the Canterbury and Manawatu-Whanganui regions, Environment Canterbury and Horizons Regional Council unpublished data). In those cases, conductivity was not significantly related to DIN. A relationship with DIN might be expected because when NO_3^- leaches from soils, it carries cations with it, especially Ca^{2+} and Mg^{2+} (Likens et al. 1970). In the Likens et al. (1970) study, a 56-fold increase in NO_3^- (from ~ 200 to $11000 \text{ mg N m}^{-3}$) corresponded to a 3- to 8- fold increase in conductivity (from 20 to 65 – 160 $\mu\text{S cm}^{-1}$). This effect of leaching would vary depending on background conductivity.

A pattern seen in the Manawatu-Whanganui region was that sites with both high conductivity ($> 160 \mu\text{S cm}^{-1}$) and high DIN ($> 480 \text{ mg m}^{-3}$) tend to have higher peak chlorophyll *a* than sites with lower conductivity but similarly high DIN and similar DRP (Horizons unpublished data). This relationship with conductivity was seen mostly clearly at sites where periphyton was readily removed by small floods. This suggests that the high conductivity sites may be more productive, or support more chlorophyll *a*-rich periphyton, than low conductivity sites, depending on DIN and DRP concentrations. In other words, sites with naturally high conductivity (e.g., from calcareous catchment geology) may be more vulnerable to developing high periphyton standing crop if DIN increases. This observation is preliminary and requires further investigation. In particular, at high concentrations (e.g., $> 1000 \text{ mg m}^{-3}$) DIN enrichment increases conductivity, and the effect of the two factors cannot be separated.

8.5 Implications of interactive effects

The two factors that exert most influence over periphyton **standing crop** in rivers are likely to be nutrient supplies (through stimulation of **growth rates** when concentrations are below the levels that saturate growth, and when other factors are not limiting growth) and flow (through removal of biomass in the scouring conditions of high flows) (Figure 4-1, and see review by Larned 2010). The effect of flow can be summarised as the “accrual period” or the time elapsed since the most recent biomass-clearing flood (Biggs 2000a). The general relationship between maximum periphyton biomass (as chlorophyll *a*), nutrients and flows can be summarised in a simple diagram of idealised accrual under different levels of enrichment (left hand plot in Figure 8-1).

Declining chlorophyll *a* following peak biomass, shown in Figure 8-1, can occur when thick periphyton mats undergo natural sloughing as algae at the base of the mat becomes senescent (e.g., Biggs & Stockseth 1998). The dotted lines in Figure 8-1 represent uncertainty. In reality, the interactions between periphyton, nutrients and the factors described in Sections 8.1 to 8.4, result in considerably higher uncertainty than depicted. Furthermore, the uncertainty extends to all parts of the idealised plots for each enrichment category. The bars on the right of the plot in Figure 8-1 represent interacting factors that could potentially change the relationships shown on the left. A combination of all the physical factors at the top of the bars could represent “hot spots” for potentially high periphyton standing crop. Conversely, the combinations of factors at the bottom represent ideal conditions for minimum chlorophyll *a*. More investigation is needed to define numerical values for each interacting factor.

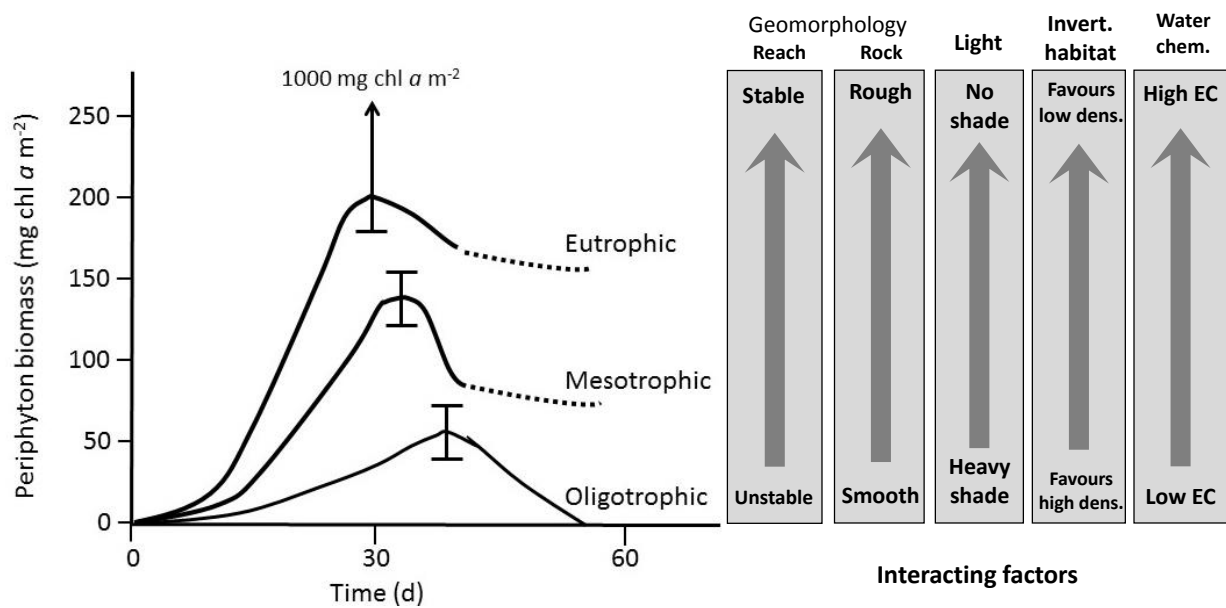


Figure 8-1: Idealised periphyton biomass accrual at three levels of stream enrichment, with potentially interacting factors shown on the right. Time (d) shows the number of days following a flood disturbance that removed biomass. Dotted lines indicate uncertainties in rates and magnitudes of biomass loss following the peak in each enrichment category. The thresholds of DIN and DRP between the three enrichment categories are not well defined but in the New Zealand context could be compared to the ranges seen in the three groups of the NRWQN shown in Table 4.1. The bars on the right show the factors that may also affect periphyton and therefore change the relationship with nutrients. Conditions associated with increasing standing crop are shown at the top, and declining standing crop at the bottom. “Hot spots” for high chlorophyll *a* potential meet the all conditions at the top of the bars. Refer to text for more details. EC = electrical conductivity. (Left hand plot from Larned et al. in press).

Figure 8-1 is an expansion of the conceptual model of the factors influencing periphyton biomass growth and loss depicted in Figure 4-1. It incorporates the effects of flow variability as well as local geology (which controls rock type and water conductivity).

The effects of interactions explain the failure of most attempts to link periphyton standing crop and nutrient concentrations through synoptic surveys across multiple sites (see Section 7). Patterns along river continua tend to be clearer (see Sections 7.1 and 7.5), because the interactive factors are more likely to be similar across sites (because they are in the same river), or to change across sites in a more predictable way.

9 Alternative or unintended sources of nutrients

9.1 Sediment-sourced DRP

In most of the above review, relationships between periphyton and nutrients have been considered under the assumption that DIN and DRP in the water column reflect N and P supplies available to periphyton. The cycling processes for both N and P include phases of transformation that could potentially provide additional nutrients (see Sections 5.1, 5.2). For N, the transformations within the anoxic compartment of the nitrogen cycle in rivers generally occur rapidly and the net effect is that periphyton do assimilate mainly N from the water column (Birgand et al. 2007, O'Brien et al. 2012). The exception is fixation of N₂ by N-fixing (diazotrophic) cyanobacteria. N-fixing taxa generally start to dominate the periphyton only when soluble N is in very low supply (e.g., Gillett et al. 2016), and are therefore rarely a concern in agricultural streams.

In contrast to N, DRP in the overlying water is unlikely to represent the total supply of P to periphyton because of the way that fluxes of the release of inorganic P from sediment-bound sources can be tied to diurnal cycles of pH and O₂ related to algal photosynthesis and respiration (Dodds 2003, Withers & Jarvie 2008). The importance of benthic recycling for periphyton in New Zealand has been highlighted recently by research showing that mats of the potentially toxic cyanobacterium *Phormidium* can dominate the bed of relatively large rivers which have extremely low concentrations of DRP. Conditions exist within *Phormidium* mats that allow this cyanobacterium to acquire P from fine sediment (Wood et al. 2014). In recent surveys in the Hurunui River, *Phormidium* dominated the periphyton at the downstream sites, where high chlorophyll *a* was attained in DRP concentrations down to < 2 mg m⁻³. The pattern of potentially bioavailable P in river sediments was consistent with acquisition of P from this source at the downstream site (Kilroy & Wech 2015).

9.2 Legacy effects

The issue of legacy effects for phosphorus is closely related to sediment-sourced nutrients. The problem was summarised by Jarvie et al. (2013) in relation to observations that strategies to reduce P loads to rivers have failed to deliver the expected river ecosystem benefits, even after many years. P-rich particles can continue to be delivered to rivers for decades after mitigation of the activities that created them (including point source and diffuse discharges) (Hamilton 2012, Haygarth et al. 2014). Periphyton growth may then become decoupled from DRP in the overlying water (see Section 9.1 above), so that nutrient limits related to chlorophyll *a* are no longer meaningful, even if they are set on the basis of sound analysis (Dodds 2007).

Legacy effects for DIN are usually tied to groundwater – surface water interactions (e.g., Baalousha 2012). Nitrate-N in particular percolates quickly to groundwater and, if the groundwater reservoir is large, considerable time (e.g., decades) can elapse before the nitrate is measurable in groundwater, and in the river systems fed by groundwater. The legacy of increased nitrate can persist for much longer (Hamilton 2012). As an example, Withers et al. (2014) described the situation in the UK, where a post-war push to increase productivity had effects on groundwater N levels that took years to appear and is expected to take generations to mitigate. Levels of P in soils increased at the same time, and are also expected to take decades to draw down. Despite the potential for stimulation of periphyton in rivers through recycling of particulate P (Section 9.1) Withers et al. (2014) expected the ecological effects of P (e.g., as increased periphyton) to be less than those of N in groundwater because of the low biological availability of soil-bound P.

9.3 Unexpected outcomes of mitigation

Efforts to mitigate the adverse effects on streams of long-term agriculture have sometimes resulted in unexpected (and unwanted) effects. As an example, increased nutrient export has also been reported as a consequence of restoration efforts. In a Waikato stream, following integrated catchment management that included stock removal and tree planting, increased concentrations of N (including $\text{NO}_3\text{-N}$) and DRP were recorded 7 years after the restoration work, compared with no detectable changes at control sites (Hughes & Quinn 2014). Suggested causes for the increased N concentrations were reduced uptake due to light limitation of periphyton, and possibly increased N export from the spread of gorse (see Section 4.2.1). No measures of periphyton were reported.

This example of long-term follow-up of the ecological effects in rivers of measures to mitigate nutrient effects from catchments appears to be relatively unusual (but see Suplee et al. 2012).

10 Effect of river size

Some of the factors controlling periphyton standing crop are controlled by river size (e.g., see Section 5.3.3). River size can be defined by stream order, and also by stream width and mean flow. In this section, these factors are summarised, focusing on the Mountain and Hill rivers defined in Section 2. The main focus is on DIN, reflecting the considerable literature located on the transport of DIN through river networks, from small headwater streams to high-order rivers (e.g., Alexander et al. 2000, 2007, Godwin et al. 2009, Goodale et al. 2009, 2015, Hall et al. 2013, Mulholland et al. 2008). Relatively little equivalent literature deals with phosphorus transport at the catchment scale. DRP concentrations in rivers are determined more by complex instream processes than by delivery from upstream (House 2003, Withers & Jarvie 2008). Therefore the role of stream size is less clear cut than for DIN. In the following the main processes affecting N and P transport and usage from small headwater streams to large lowland rivers are briefly reviewed.

10.1 Nitrogen transport and usage through river networks

The nitrogen that moves through river systems and affects periphyton growth rates and standing crop is mainly in soluble form (DIN, comprising $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$). DIN uptake rates are determined by background concentrations in the water column and processes at the stream bed (see Section 5.3.3). Rates increase as concentration increases (Dodds et al. 2000). The proportion of N retained in the stream (e.g., as periphyton biomass) is higher in small, shallow streams because the area of bed relative to water volume is low (see Section 6.3.1). Therefore small streams, which in New Zealand can have very low DIN concentrations when they are in undeveloped catchments (see Sections 2 and 6.1), are often very effective at removing N (Alexander et al. 2000). However, this applies only up to moderate concentrations (e.g., $\sim 100 \text{ mg m}^{-3}$); once concentrations increase past $\sim 1000 \text{ mg m}^{-3}$, it appears that neither small nor large rivers retain significant amounts of DIN. In this case, DIN-enriched small streams can collectively contribute disproportionate loads of DIN (predominately $\text{NO}_3\text{-N}$) to higher order streams (Alexander et al. 2007, Mulholland et al. 2008), but continue to support high periphyton standing crop (assuming other factors such as DRP and light are not growth-limiting) (Figure 10-1).

10.1.1 The effect of shading

Heavy shading over a stream generally overrides the effect of nutrient additions and may therefore reduce the potential for development of high periphyton biomass (although in some cases, periphyton may adapt to shade, see Section 8.2). Riparian shading can be effective only in narrow waterways. According to Davies-Colley & Quinn (1998), the stream width limit, on average, is about 5 m. This assumes tall tree cover that blocks out over 95% of incident light. In a 5-month experiment in streamside channels, chlorophyll *a* consistently remained $< 17 \text{ mg m}^{-2}$ under $< 10\%$ PAR, and exceeded 30 mg m^{-2} only once under 40% PAR. With no shading (100% PAR) chlorophyll *a* exceeded 50 mg m^{-2} on several occasions in late summer (Quinn et al. 1997). The interaction between shade and nutrient export, and between river size and nutrient export, leads to a situation whereby the effect of shade in mitigating periphyton biomass is without risk only when DIN concentrations are high (e.g., well over 100 mg m^{-3}). The effect is shown in Figure 10-1. Periphyton standing crop is predicted to reduce (relative to unshaded sites), with no change to already high DIN export, only at high DIN. At low DIN, we expect that periphyton will be low through nutrient limitation. At moderate DIN, periphyton may decline, but nutrient export increases.

10.1.2 Invertebrate habitat

The effect of invertebrate grazing (where it is occurring) should be evident in wadeable areas in any river, regardless of size. The difference linked to river size arises from the fact that any actions to improve habitat for invertebrates are likely to be effective only in small streams (Greenwood et al. 2012). In small streams, large proportions of the stream bed can be targeted for structural changes that have potential to both increase densities of grazing invertebrates and possibly enhance loss of DIN from the system to help reduce export to downstream reaches (Craig et al. 2008). Such changes include: channel widening and introduction of meanders (which create localised riffles with increased water velocities as well as areas with slower flows); and addition of wood debris / debris dams (which would increase velocities in places, and trap sediment in localised areas, as well as providing carbon for potentially enhancing denitrification).

Improvements to invertebrate habitat would be expected to have maximum impact in small, unshaded streams with moderate nutrient concentrations (Figure 10-1).

10.2 Phosphorus transport and usage through river networks

Phosphorus differs from nitrogen in that much of its delivery to and transport through river networks occurs in insoluble particulate form (see Section 5.2). Concentrations of DRP in the water column may represent only a proportion of P that is directly available for uptake by periphyton. P availability for algal growth may depend as much on site-specific processes as on direct delivery from upstream (House 2003). Exceptions include sites downstream of wastewater treatment plants where P discharges to rivers occur mostly as DRP (e.g., Bowes et al. 2011).

At the catchment scale, a smaller proportion of the inputs of P onto arable agricultural land use may find its way into rivers than for N (e.g., ~2% compared to 16% in the Mississippi River basin, Alexander et al. 2008). The opposite may be true for pasture-based agriculture (e.g., 14% vs. 6% for P and N respectively, Alexander et al. 2008). To offset downstream delivery of P, lakes, reservoirs and floodplains in catchments can trap P (in particulate form) to a much greater extent than for N (Nemery & Garnier 2007, Alexander et al. 2008). Trapping of P can also occur within the stream channel in areas of slow water velocity (Ensign & Doyle 2005).

Most downstream delivery of P occurs during high flows through export of P bound to sediment or in organic form (and measured as TP) (e.g., Nemery & Garnier 2007). These authors reported increasing P content in suspended sediment in a downstream direction in the Seine catchment (France) with four times as much P per unit sediment weight at the catchment outlet (with high agricultural influence) compared to headwaters (with low agriculture). A similar pattern has been detected across New Zealand rivers using data from the NRWQN sites (McDowell & Hill 2015), and within single catchments (e.g., Kilroy & Wech 2015).

In small headwater streams in pristine catchments, DRP recycling can be very rapid, as reflected by short uptake lengths (see Section 5.3.2) compared to longer uptake lengths for DIN (Ensign & Doyle 2006). Thus, stream size influences the uptake of DRP in the same way as for DIN: small headwater streams have a greater stream surface area relative to water volume, and therefore greater capacity for DRP uptake and P transformations at the bed than larger, high-order rivers. However, relationships between DRP in the water column and assimilation into periphyton standing crop are not straightforward. For example, the role of bacteria in recycling P into forms that are available for uptake by algae has been shown to be more pronounced in streams with low background P concentrations than with high background P (Scott et al. 2008).

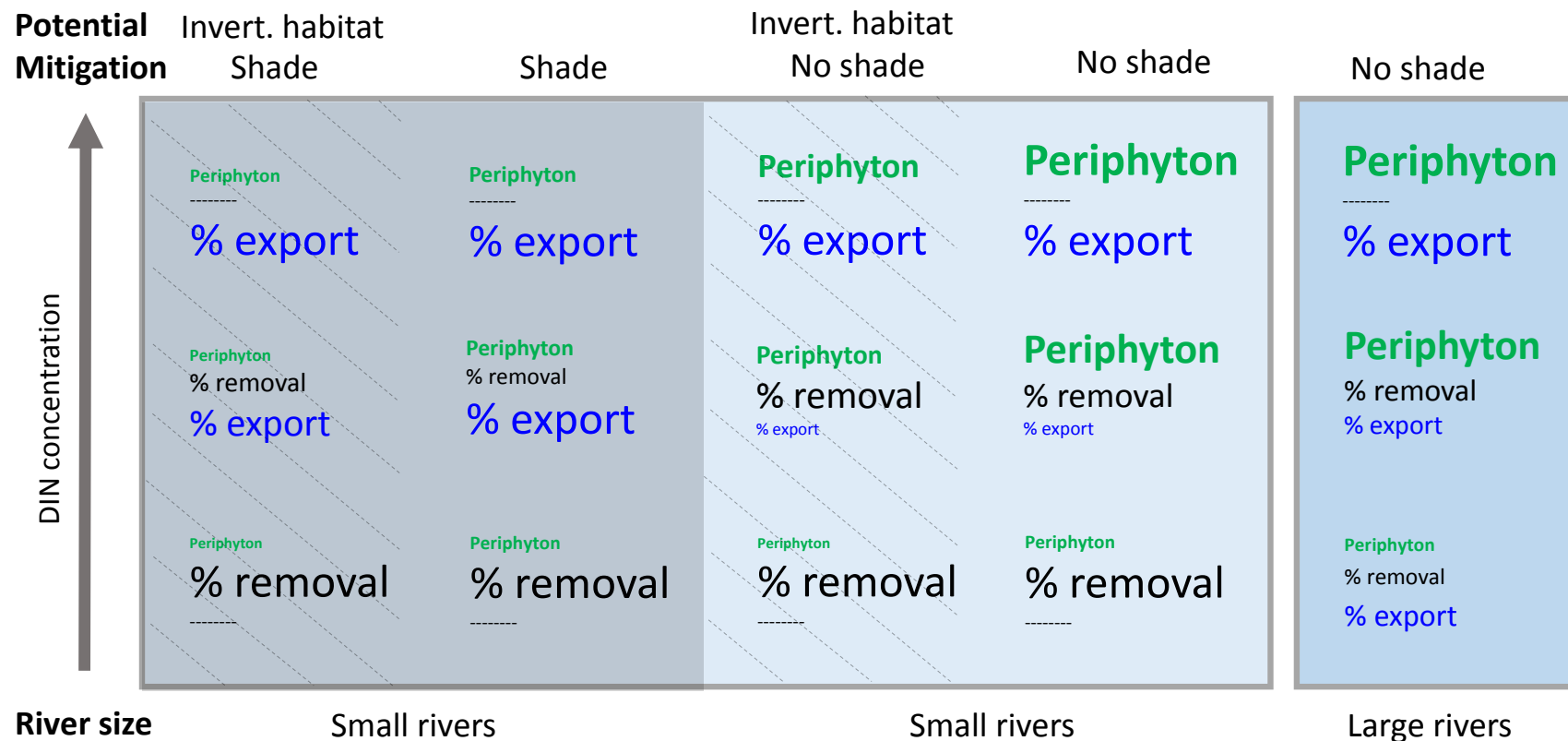


Figure 10-1: Diagram of relative periphyton standing crop and percentage removal and export of N at different N concentrations in large and small rivers. Font size represents the relative magnitudes of periphyton standing crop (in green), export of N downstream (in blue) and removal of N within the reach (in black). Removal refers to the combination of biological uptake and other N loss processes including denitrification. Horizontal dashed lines indicate no measurable export or no removal.

The potential effects of two possible mitigation measures are shown: grey shaded areas show effects of adding riparian shade; hatched areas show effect of carrying out instream physical habitat improvement for invertebrates that is also expected to enhance DIN removal by other means (see Craig et al. 2008, Greenwood et al 2012).

The threshold separating small and rivers is approximately $0.1 \text{ m}^3 \text{ s}^{-1}$, based on Mulholland et al. (2008). The width of a small river is up to ~ 5 metres (Davies-Colley & Quinn 1998). DIN is shown on a relative scale only. Mulholland et al. (2008) suggested a range of $\text{NO}_3\text{-N}$ from <10 (low) to $> 1000 \text{ mg m}^{-3}$ (high concentration), but this range may need to be adjusted for New Zealand conditions.

Literature comparing the relative importance of transport, uptake and retention of P according to stream size appears to be lacking (Withers & Jarvie 2008). Generalisations such as those made for NO₃-N or DIN (Mulholland et al. 2008, and Figure 10-1) may not be possible for P because of the dependence of P cycling processes on specific conditions in individual rivers (House 2003, Scott et al. 2008). In addition, catchment geology, which affects water chemistry and river geomorphology, influences mechanisms of P processing (reviewed by Withers & Jarvie 2008), complicating the prospects for models applicable across multiple rivers.

11 Predicting and managing periphyton

Two questions are addressed:

1. How predictable is periphyton (as chlorophyll *a* or cover) from nutrient concentrations?
2. What are the prospects for successful management of streams to ensure maintenance of periphyton chlorophyll *a* at acceptable levels (i.e., to a maximum of < 200 mg m⁻² no more than once per year, based on monthly monitoring – or staying better than Band D in the NPS-FM)?

11.1 Predictability of periphyton

The algae that make up most of the biomass of periphyton have absolute requirements for N and P. Therefore, if all other conditions were equal, the growth rate and growth potential of an algal species should be predictable from the amount of N and P available (as shown in the left hand plot in Figure 8-1). However, in rivers, all other conditions are never equal. This review has highlighted great variability in periphyton chlorophyll *a* across different ranges of DIN and DRP concentrations in different regions (Section 7). River flow and geomorphology, light, invertebrate grazing, and water chemistry were highlighted as major factors that can influence periphyton standing crop (Section 8).

To date, the most successful attempt to relate periphyton chlorophyll *a* to nutrient concentrations across a range of sites was the study by Biggs (2000a). Variability over time in DIN, DRP and chlorophyll *a* was accounted for by calculating mean or maximum values from at least 12 monthly surveys. It is also probable that the rivers included in the dataset were relatively homogenous in terms of their general characteristics. Equivalent regional datasets from monthly surveys are now available, and work is underway to develop regional relationships. Models capable of making accurate site-specific predictions of chlorophyll *a*, and which improve on the Biggs (2000a) relationships, are still proving elusive but recent research is providing some bases for categorising sites to improve predictability (Hoyle et al. in press). On the other hand, it is already possible to make reasonably accurate regional-scale predictions about periphyton abundance, such as proportions of sites exceeding certain criteria (Snelder et al. 2013).

At the scale of a river, relationships between chlorophyll *a* and nutrient concentrations were usually clearer because the sites along a river tend to have features in common. One example was provided of a case where strong DIN and slight DRP gradients drove a change in periphyton taxonomic composition rather than chlorophyll *a* (Gillett et al. 2016). Overall, the review indicated that useful models might be possible at the catchment scale (e.g., Suplee et al. 2015).

11.2 Prospects for management success

In theory, where DIN or DRP concentrations are initially in excess of those thought to saturate their incorporation into periphyton, and maximum standing crop is high (e.g., exceeds guidelines), then reductions in maximum periphyton standing crop can only occur following reductions in DIN and DRP to below saturating concentrations. These concentrations may be 230 – 280 mg m⁻³ for DIN and around DRP of ~28 mg m⁻³ for DRP (see Section 6.4). There is uncertainty about the general applicability of the saturating thresholds because it is unclear whether they were derived in conditions under which no other factors were limiting periphyton growth. Nevertheless, the DIN threshold range is well above the median value for rivers classed as Baseline sites in the NRWQN (Table 6-1), indicating that DIN at many New Zealand sites is still below concentrations associated

with high chlorophyll *a* (but see Larned et al 2016 for a more comprehensive analysis). However, median DIN values at NRWQN impacted sites exceed the suggested thresholds for saturation (see Table 6-1). Mean percentage cover by filamentous algae at these sites was also relatively high, being around 30% cover (Table 6-3). Maximum cover by filamentous algae of 30% was the threshold for maintenance of aesthetic/recreational and trout habitat/angling values in the 2000 NZ Periphyton Guideline (Biggs 2000b).

It should be noted that the rivers in the NRWQN are biased towards upland, relatively unimpacted, upland rivers (Davies-Colley et al. 2011, Larned et al. 2004). Also note that many of the NRWQN sites have large seasonal fluctuations in DIN, therefore the thresholds representing potentially growth saturating DIN may be exceeded at many sites for at least part of the year.

The literature-derived concentration of DRP (28 mg m^{-3}) above which maximum periphyton standing crop no longer increases was much higher than those for DIN, relative to concentrations at NRWQN sites. Median DRP exceeded 28 mg m^{-3} at only three of the 77 sites, all in the North Island. Across 320 lowland sites, which are more likely to be affected by agriculture, median DRP was 16 mg m^{-3} (Larned et al. 2004). The implication is that P rather than N may limit periphyton standing crop at many New Zealand sites. Consequently, reducing DRP concentrations in rivers might be expected to lead to reduced peak periphyton standing crop. At the same time, slight increases would increase the risk of higher peak chlorophyll *a*. However, numerous studies have shown that DRP in the water column is not the sole source of bioavailable P in freshwaters (Dodds 2003, Ellison & Brett 2006, McDowell et al. 2016). The ability of periphyton to make use of P bound to sediment or recycled within thick mats means that reductions in DRP through management actions may not have the expected effect of alleviating nuisance periphyton (Jarvie et al. 2014; and see Section 9.2).

Only one study was located in which chlorophyll *a* was measured over a long time period to assess the response to nutrient reductions. The outcome of that study was that declining TP was associated with declining chlorophyll *a* at several sites where TP fell below the level thought to be linked to growth saturation (Suplee et al. 2012).

In general, the overall success rate for mitigation of the effects of nutrient inputs (and other changes) in rivers appears to be low (Harris & Heathwaite 2012), but the lack of success may be more to do with lack of appropriate evidence to demonstrate success than failure of the mitigation. In other words, even when monitoring is carried out, the information obtained is often inadequate to judge the success or otherwise of the measures (Berhardt & Palmer 2011). Thus, robust sampling and monitoring procedures are critical for both identifying relationships between periphyton and nutrient concentrations, and for confirming the outcomes of efforts to mitigate and manage nutrient inputs (see Section 4.2).

In this report Figure 10-1 is presented as a prototype template to guide the feasibility of applying mitigation measures to assist with compliance with the NPS-FM, in particular ensuring chlorophyll *a* < 200 mg m^{-3} (see footnote 3, Section 3.3), in relation to DIN. Figure 10-1 shows that:

- mitigation of DIN and periphyton in large rivers needs to start with management of inputs from small rivers;
- using shading as a method of reducing periphyton standing crop in small streams with slightly elevated DIN may result in more DIN to be exported downstream;

- It is possible that stream restoration to enhance habitat for invertebrates (e.g., create faster flows and minimise fine sediment inputs) could both reduce periphyton AND mitigate export of DIN, through increasing recycling at the reach scale. This is probably most effective in unshaded reaches, where periphyton growth (and therefore uptake of DIN) is not limited by low light;
- at very high DIN (well over standing crop-saturating concentrations), and in all rivers regardless of size, net uptake of DIN as a proportion of the DIN available (including uptake by periphyton and denitrification) is low. Recycling of DIN predominates and most DIN is exported. In that case, direct steps to reduce DIN inputs to the waterway are the only options for mitigation.

Evidence for the success of instream physical restoration aimed at reducing DIN export (through enhancing within-reach uptake, including by periphyton) is limited (Filoso & Palmer 2011). These authors concluded that meaningful reductions in DIN export would generally require measures more drastic than stream restoration or habitat enhancement. For example, an ecosystem change might be required, such as from a stream to a constructed wetland, where periphyton standards would no longer apply. Such large changes would need to be acceptable to local communities.

Berhardt & Palmer (2011) cautioned that small-scale restoration or habitat enhancement “should not be expected to alleviate problems generated throughout a catchment” and that effective restoration would first focus on the catchment sources of excess N or P. Nevertheless Berhardt & Palmer (2011) concluded by expressing optimism about the impacts of increased understanding of the difficulties involved in reversing the effects of nutrient inputs, suggesting that: “... structural enhancements within the stream channel will likely be necessary to create and reinstate appropriate habitat diversity.” In that case, potential interception of even small amounts of DIN through the restoration of stream reaches could be considered as a positive step because of the accompanying improvement to the stream habitat.

In some cases purpose built-filamentous algae nutrient scrubbers (FANS; Sutherland & Craggs 2016) could be appropriate. Such manipulations may be possible in small streams with the aim of limiting periphyton standing crop in downstream runs so that chlorophyll *a* stays below the bottom line set by the NPS-FM.

The DIN concentrations in Figure 10-1 are based on literature values, which were presented on a log scale (Mulholland et al. 2008). The thresholds of DIN in New Zealand rivers below which it may be feasible reduce concentrations through instream manipulations are currently unclear and require research. However, calculations of the capacity of DIN uptake (*U*) to reduce concentrations could assist (see Section 7.3.2). The aim of instream management is to maximise *U*, while still controlling chlorophyll *a* (see Figure 8-1).

12 Synthesis and conclusions

This review has explored periphyton – nutrient relationships, with a focus on New Zealand rivers, with the eventual aim of providing Dairy NZ with an information source for addressing queries about the consequences of land use management changes on rivers. The review focussed on **periphyton standing crop** in cobble-bed rivers, usually measured as **chlorophyll *a*** (the measure used in the NPS-FM periphyton attribute). Concluding messages from the review follow.

- Nutrient supplies (N and P) are fundamental drivers of algal **growth rates**: increasing concentrations of nutrient = higher growth rates, up to the point where nutrient concentrations are saturating. This assumes that neither N, P nor other factors (such as light and micronutrients) are in such low supply that they limit growth.
- The role of N and P in influencing periphyton **standing crop** (as opposed to algal growth rates) is not always clear in studies on periphyton in rivers, unless the influence of other controlling factors is accounted for.
- River flows (in particular, the frequency of high flows that remove periphyton biomass) are the most important influence on periphyton standing crop over time.
- The strong influence of hydrological conditions on periphyton standing crop means that time-series studies are usually necessary for estimations of peak standing crop. Use of estimates of peak standing crop can lead to identification of clearer relationships between nutrients and periphyton.
- Survey location and sampling techniques can influence periphyton – nutrient relationships, and these were also considered in the review.
- Cycling and downstream processing (spiralling) of N and P were reviewed. Biological uptake (by periphyton) accounts for major portions of nutrient removal from stream waters. However, few studies were located in which uptake rates were compared with periphyton standing crop.
- Most New Zealand rivers show seasonal fluctuations in dissolved N and P, with annual maxima in DIN in winter and minima in mid-summer. Fewer rivers showed seasonal patterns in DRP. The seasonal patterns in DIN are likely to be at least partly driven by seasonal flow patterns, but other processes (including catchment and instream uptake, and N-fixing vegetation) likely drive seasonality at some sites.
- Studies were reviewed of periphyton in relation to N and P at multiple sites along the same river, and in surveys at sites in different rivers and catchments in the same region.
- In 14 longitudinal studies in New Zealand and overseas, periphyton chlorophyll *a* gradients along rivers generally corresponded to N and P gradients, regardless of survey location and sampling technique. However, the absolute values of chlorophyll *a* linked to different N and P concentrations varied across rivers.
- In eight between-river studies, only one synoptic survey of multiple sites in different rivers and catchments showed strong relationships between periphyton standing crop (as chlorophyll *a*) and nutrient concentrations. Lack of relationships between

periphyton and nutrient concentrations was explained site characteristics in at least three studies.

- The single between-river study that included time-series data showed relatively strong nutrient relationships between maximum chlorophyll *a*, and time-averaged nutrient concentrations. Adding a term to account for accrual period improved the relationships.
- Little information was located on the effects of seasonal changes in nutrient concentrations on chlorophyll *a*, probably because these seasonal changes often coincide with flow changes, which have an overriding effect on periphyton.
- The effect of periphyton on removal of nutrients from the water column was evaluated using published uptake rates. The conclusion was that, despite the prominence of biological processes in nutrient uptake in streams, removal is generally negligible except in long periods of declining water depth over long, shallow, stream reaches, when starting concentrations are low.
- Few studies examined chlorophyll *a* versus nutrient concentrations over long periods (as opposed to seasons). The best example was a study at multiple sites on a single river over 12 years. Management-led reduction of P resulted in chlorophyll *a* reductions at sites where P fell below saturating concentrations.
- Saturating concentrations of DIN and DRP (i.e., above which periphyton standing crop no longer increases) were suggested in some studies. Estimates for DIN were 230 – 280 mg m⁻³, on average, although uncertainty around these averages is high. The corresponding values for DRP appears to be ~28 mg m⁻³. Maximum chlorophyll *a* corresponding to the suggested saturating concentrations appears to be variable, ranging from (on average) ~100 to ~350 mg m⁻². There is evidence in the literature that there may be regional differences in saturating concentrations.
- The chlorophyll *a* threshold defining the bottom line in the NPS-FM (200 mg m⁻²) was exceeded at DIN from 170 to 4000 mg m⁻³ and DRP from 5.7 to > 70 mg m⁻³, indicating great variability across rivers.
- Four factors that have interactive effects on periphyton – nutrient relationships were reviewed. These were: geomorphology (at the reach scale and rock scale), shading, invertebrate grazing, water chemistry. Each of these factors may significantly modify how periphyton standing crop responds to nutrient enrichment. An idealised model is presented for assessment of sites that may represent “hot spots” for high periphyton standing crop. More investigation is needed to define numerical values for each interacting factor.
- Although most supplies of nutrients to periphyton are from the water column, sediment can be a significant source of P. P from this source can represent a long-term legacy from past land-use practices, maintaining high standing crop despite low DRP concentrations in the water. Legacy-sourced DIN (from groundwater, or, in one example, as an unexpected outcome of catchment management) may also delay positive effects of current nutrient management.

Information from the review was used to evaluate the effect of applying measures to reduce periphyton standing crop on small rivers. Feasible methods are introducing shade and modifying habitat to promote invertebrate grazing.

- A conceptual model shows that maximum benefit (i.e., lower periphyton biomass, while minimising DIN export to downstream reaches) is most likely if invertebrate grazing can be promoted in unshaded small rivers with moderate DIN concentrations.
- This evaluation in effect identifies further “hot spots” in rivers that could be targeted and managed for maximum removal of nutrients from the water column, specifically small, unshaded streams with good habitat for invertebrates (i.e., fast-flowing riffles).
- At this stage the literature indicates that mitigation attempts may be ineffective in both small and large rivers where DIN concentrations are already high (e.g., > 1000 mg m⁻³). Therefore taking direct steps to reduce DIN inputs to the waterway may be the only option for reducing periphyton chlorophyll *a* in these cases. However, the threshold of DIN below which mitigation (i.e., controlling chlorophyll *a* in relevant parts of the river, while minimising DIN export) may be possible is unclear, and requires further research in New Zealand.
- Generalisation of steps to reduce DRP availability to periphyton in streams is more complex than for DIN. A high proportion of DRP is delivered to streams in particulate form, from which algae can access P directly under certain conditions. The mechanisms for accessing P vary according to water chemistry and river geomorphology.

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