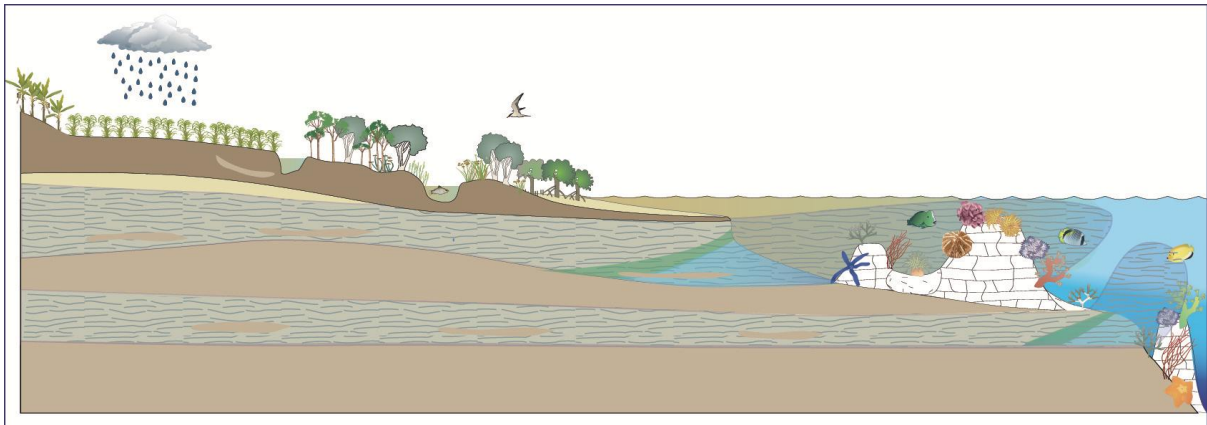


Nutrients and herbicides in groundwater flows to the Great Barrier Reef lagoon

Processes, fluxes and links to on-farm management



Heather M. Hunter

September, 2012

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The full set of illustrations presented in the report may be downloaded from the following website; each illustration includes a title for use independently of the report: www.reefwisefarming.qld.gov.au/

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Context to the report

The Queensland Government's Reef Protection Program provided funding for an up to date review and synthesis report to inform the scientific and monitoring work underpinning the Reef Plan. This resultant report will inform discussion around investment and monitoring priorities as well as identify where additional activity is required to provide guidance for on-farm mitigation.

The Queensland Government is committed to ongoing investment in Reef Protection science and as new information becomes available, government policy will be adapted to take account of it. The report is provided in good faith on the understanding that the information is not used out of the context explained above.

Executive Summary

A key objective of the Reef Water Quality Protection Plan (Reef Plan) is to reduce the amounts of nutrients and herbicides entering the Reef from its catchments. To date, Reef Plan actions aimed at mitigating the transport of these contaminants to the Reef have focussed on surface water processes and pathways of delivery, while the role of groundwater in the transport of these contaminants remains poorly understood.

The purpose of this study was to provide an up-to-date review and synthesis of current knowledge on groundwater transport to the Reef of nitrogen (N), phosphorus (P) and herbicides (specifically, those that act by impairing photosynthesis, hereafter called ‘PSII herbicides’). The review was guided by the following three priority needs, to; i) inform policy development; ii) identify options for on-farm mitigation; and iii) ensure Paddock-to-Reef scale monitoring, modelling and reporting programs account for groundwater discharges of these contaminants. The geographic scope of the review was on sugarcane production areas in coastal parts of the Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas.

Specific objectives of the study were to review and assess:

- Current knowledge of aquifers and groundwater processes across the study areas, including groundwater–surface water interactions, and spatial and temporal patterns of water level fluctuations and groundwater flows
- The recorded presence of N, P and PSII herbicides in groundwater in the study areas
- Processes that underlie transformations and attenuation of these contaminants in the root zone and deeper subsurface environments, their transport to the Reef lagoon, and the links to on-farm management
- The relative importance of groundwater flows of N, P and PSII herbicides to the Reef lagoon from the study areas, relative to surface water flows
- The need for enhancement of current Paddock-to-Reef (P2R) monitoring, modelling and reporting programs to take account of nutrient and herbicides transported via groundwater pathways
- Critical knowledge gaps that need to be addressed so that effective mitigation and monitoring strategies can be devised and implemented.

The review provides a brief overview of current knowledge of aquifers and groundwater processes across the Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas. Unconfined alluvial aquifers are widely represented across the study areas, with confined or semi-confined alluvial aquifers and fractured bedrock aquifers also present in some systems. Marked seasonal fluctuations in groundwater levels are common, but longer-term trends for rising groundwater levels are evident in some aquifers, particularly in parts of the lower Burdekin. There is a high degree of connectivity between groundwater and surface waters in each study area, with considerable groundwater discharge occurring to riverine environments and to the coast. Artificial drains have been constructed in some areas to lower watertables rapidly in wet weather and prevent waterlogging of cane crops.

Submarine groundwater discharge (SGD) directly to the coast has been identified and mapped at numerous locations along the Wet Tropics coast and in Bowling Green Bay (in the lower Burdekin) but has been quantified only in Bowling Green Bay. SGD has not yet been identified or mapped in the Mackay–Whitsunday area. Similarly, groundwater discharge to rivers and streams has been quantified (at the end of the wet season) in the lower Burdekin, but has not been quantified elsewhere in the three study areas. However, middle and lower sections of rivers in the Wet Tropics have been broadly identified as receiving considerable amounts of groundwater discharge, while shallow groundwater discharge has been documented to streams and drains in both the Mackay–Whitsunday and Wet Tropics areas. Overall, the estimated mean annual total groundwater discharge from each of

the main aquifers is <10% of mean annual discharge from the corresponding river system. Based on draft water balance estimates, groundwater discharge to rivers, streams and wetlands in the Wet Tropics far outweighs groundwater discharge to coastal parts of the Wet Tropics. By contrast, draft estimates for the lower Burdekin and Mackay–Whitsunday areas suggest that almost as much groundwater discharges directly to the coast, as to rivers and streams.

The review also assesses information available on the recorded presence of N, P and PSII herbicides in groundwater in the three study areas. In general, while there is considerable information on nitrate levels in groundwater, relatively little information is available on P, herbicides, or other forms of N, particularly for the last ten years. However, two recent studies in the lower Burdekin are important exceptions, in which nutrients and herbicide residues were monitored strategically at groundwater locations close to potential riverine and coastal discharge zones. Only low concentrations of nutrients and several herbicides were detected. Further monitoring in the lower Burdekin floodplain is now following up on aspects of this initial work, funded by the Reef Protection Program. Analysis of long-term groundwater nitrate records for the lower Burdekin indicates that nitrate concentrations appear to be increasing with time. Current rising trends for nitrate in groundwater have similarly been reported for the Pioneer and Herbert areas. The most recent information on P levels in groundwater is from an Australia-wide survey of major agricultural areas in the mid-1990s, which reported relatively high concentrations of P in groundwater in the lower Burdekin and the Pioneer Valley.

Fourteen conceptual models developed in conjunction with the review summarise important aspects concerning the fate of N, P and PSII herbicides in the root zone and deeper subsurface environments. Collectively, they link key processes and pathways, from farm scale to the Reef. Leaching and deep drainage of N to groundwater mainly occurs as nitrate. Denitrification – the microbial conversion of nitrate to dinitrogen (N₂) and nitrous oxide (N₂O) gases – is a primary mechanism for removing nitrate from subsurface environments. It requires anaerobic conditions and the presence of dissolved organic carbon (DOC), although reduced forms of iron, sulfur or manganese, if present, may be alternatives to DOC. Typically, little leaching of P occurs except in sandy soils, or when soils are overloaded with P. Any P leached to groundwater potentially may be sorbed onto clay sediments or precipitated as mineral forms, some of which may subsequently release P, particularly under anaerobic conditions.

Five PSII herbicides are used in cane-growing areas of the Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas: ametryn, atrazine, diuron, hexazinone and metribuzin (although the use of diuron is currently suspended for certain high risk periods and is under review). The chemical properties of these compounds have a major influence on their fate. Within the root zone they may retain their efficacy for some time, or they may be subjected to microbial or abiotic degradation into breakdown products that may or may not retain herbicidal properties. To varying extents these herbicides may be sorbed onto soil organic matter or onto clay minerals, which can influence the extent of leaching and deep drainage. However, there is only limited information available on the sorption properties of PSII herbicides in Australian soils. Soil properties, irrigation management, the amount of herbicide applied and the timing of applications relative to rainfall and irrigation can also have a major bearing on the extent of leaching. Microbial degradation/transformation is considered the primary mechanism for herbicide attenuation in soils and deeper subsurface environments, and it is influenced by factors such as temperature, pH, redox conditions and the nature and amount of DOC present. Abiotic degradation of herbicides can also be important in anaerobic environments.

In general, key determinants of the flux of N, P and PSII herbicides through aquifers to streams and coastal waters are: the supply rate of these contaminants from the soil surface via deep drainage; redox conditions in subsurface environments; the residence time of groundwater within aquifers, the extent of contact with clay sediments; and the availability of DOC (and/or in the case of denitrification, alternative sources of electrons). However, the fate of these contaminants in subsurface environments is site specific and difficult to measure or predict due to the heterogeneous nature of aquifer sediments and the many factors involved.

Enhanced N fertiliser management is a key strategy for minimising deep drainage losses of N, with the ‘block target yield’ approach offering the potential to fine-tune N application rates while maintaining yields. Current research is investigating the potential for ammonium-based fertilisers to improve N-use-efficiency by cane and reduce off-site N losses. Most cane-growing soils in the Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas have a high P fertility status and do not require the addition of P fertiliser or organic amendments enriched with P (e.g., mill mud).

Present indications suggest that in most cases groundwater fluxes of contaminants to the Reef lagoon may be relatively small compared with those discharged by rivers. However, potentially they may have a disproportionate impact on the environmentally sensitive and highly diverse ecosystems in receiving environments along the coastal margins and in riverine environments. Exposure of these ecosystems may be exacerbated because groundwater discharges may persist through the drier months, when river flows are relatively low, and circulation patterns tend to restrict the extent of mixing of near-shore waters within the Reef lagoon. The degree to which these ecosystems are exposed to contaminants in groundwater inflows are at present unknown, as are the associated risks posed to their natural functions and values, and the potential they may offer to mitigate contaminant loads.

The P2R monitoring, modelling and reporting program has eight ‘end-of-system’ stream sampling sites in key catchments across the study areas, and a further site at the end of a major sub-catchment. Information currently available suggests that samples taken at these sites generally would not adequately account for any contaminants in groundwater inflows from aquifers to respective river systems. Enhancements to the P2R monitoring and modelling programs may therefore be required. Initial requirements include identification of locations and patterns of groundwater discharge in each of the monitored catchments, and determination of the appropriate spatial coverage and sampling times needed to adequately capture groundwater inflows. A key aim of the P2R program is to determine changes in water quality entering the Reef lagoon as a result of improvements to land management practices. The inevitable lag times between implementing on-farm changes and detecting a response at the end of a large catchment are exacerbated when groundwater processes are involved, as these may take decades to respond.

It is clear from the information presented in the review that there are very many gaps and uncertainties in our present knowledge. Given the extent of these uncertainties, it is not yet possible to assess with confidence the importance of groundwater flows of N, P and PSII herbicides to the Reef lagoon, relative to surface water flows. Nevertheless, the evidence available suggests the possibility that significant groundwater fluxes of these contaminants may occur, although the extent of their attenuation prior to discharge is not currently known. However, it should be acknowledged that there is a considerable body of valuable information now available, including from several recent studies that have significantly advanced our understanding of various aspects of these topics. Further research now in progress will add to that knowledge base, although considerably more research is required. A staged approach is envisaged to address these knowledge gaps, which would include periodic re-evaluation of the key issues and gaps as new information becomes available, and reappraisal of the relative importance of groundwater flows of these contaminants to the Reef lagoon. Key gaps are summarised below, grouped into four inter-related topics; they are not listed in any order of priority. It should be noted that addressing some of these gaps may present significant challenges.

1. N, P and PSII herbicides in groundwater flows to the Reef lagoon

- Volumes of groundwater flows (directly to the coast and to rivers/streams); seasonal patterns of discharge (and comparisons with river discharge); pathways / residence times of groundwater flows
- Concentrations of N, P and PSII herbicides in groundwater at (or as close as possible to) points of discharge
- Age of groundwater discharged and likely source/s of contaminants (if present)

2. Receiving environments of groundwater discharge
 - Identification of specific coastal and riverine locations where groundwater is discharged
 - The presence of critical ecosystems in these receiving environments; the extent of their dependency on groundwater; the ecosystem services they provide; and the threats to their functions and values from contaminants in groundwater
 - The potential of these receiving environments to mitigate contaminant loads, and the need for their conservation or rehabilitation
3. Contaminant transport, transformation and attenuation processes
 - Understanding and quantification of key processes affecting the fate of contaminants in subsurface environments and the implications for loads discharged via groundwater flows, including
 - spatial/temporal dynamics of key geochemical constituents and processes in aquifers (e.g., nitrate, PSII herbicides, Eh, DOC, Fe²⁺, S²⁻)
 - the distribution of soils in the Wet Tropics with anion exchange capacity at depth and the loads of nitrate currently held at depth in agricultural areas
 - sorption characteristics of PSII herbicides on agricultural soils
 - effects of fluctuating or rising groundwater levels on contaminant loads in groundwater discharges, and options for mitigation
 - The potential for improved on-farm management of nutrients and herbicides to reduce losses in deep drainage, while maintaining crop yields
4. P2R monitoring, modelling and reporting program
 - In each monitored catchment, identification of locations and seasonal patterns of groundwater discharge, and levels of contaminants in groundwater discharged (as in 1 and 2, above)
 - Additional monitoring (sites, sampling times/frequencies) required to ensure groundwater fluxes of contaminants are adequately represented in estimates of contaminant fluxes from monitored catchments to the Reef lagoon
 - Additional modelling capability needed in conjunction with the above

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1. Introduction

1.1 Background

Improving the quality of water entering the Great Barrier Reef (GBR) World Heritage Area is a primary and immediate goal of the Reef Water Quality Protection Plan (Reef Plan) (The State of Queensland 2009a). A key objective of the Plan is to reduce inputs of land-derived contaminants, particularly nutrients, pesticides and suspended sediment, which are present in Reef waters at above-natural levels considered likely to cause environmental harm. To date, Reef Plan actions aimed at mitigating the transport of nutrients and pesticides to the Reef lagoon have focussed on surface water processes and pathways of delivery. The role of groundwater in the transport of these contaminants is at present poorly understood (Brodie et al. 2008).

Groundwater is a critical component of the water cycle and a valuable resource. The GBR catchment lies within the Tasman Groundwater Province and includes more than twenty separate Groundwater Management Units, with groundwater used for irrigation, urban, industrial, livestock and rural domestic purposes (ANRA 2000). The importance of protecting groundwater ecosystems is now recognised, and critical knowledge gaps on this topic (amongst others) are being addressed under a major initiative of the National Water Commission (NWC 2008). As highlighted by the NWC, issues concerning groundwater and surface water connectivity, managing risks to groundwater quality, and the vulnerability of groundwater-dependent ecosystems, are central to understanding and managing linkages between land-derived sources of contaminants, their accession to groundwater and their transport to receiving environments such as the Reef lagoon.

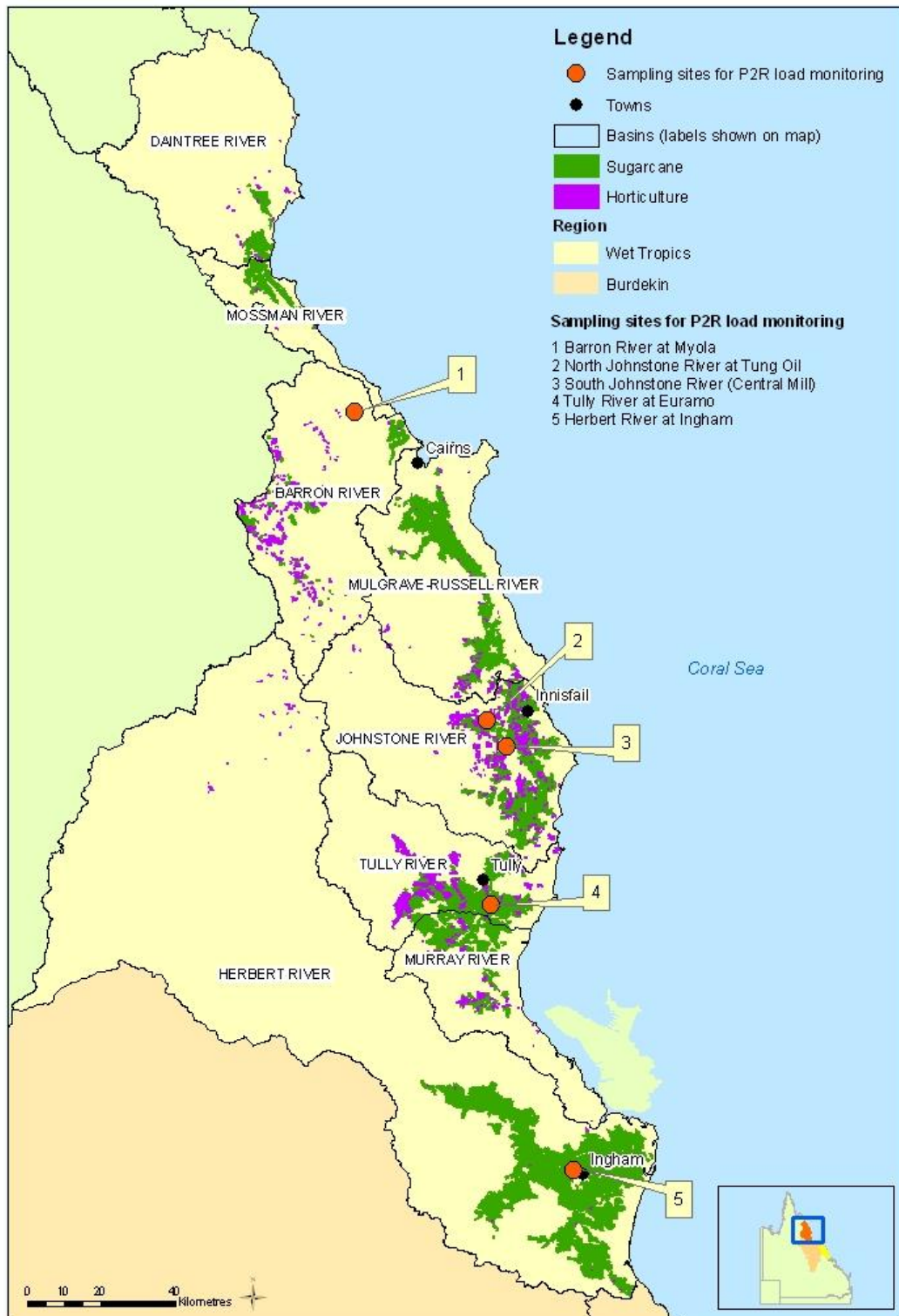
Sugarcane is the major crop grown in the GBR region, with cane produced for crushing in 2009-10 contributing \$1,264 million to the national economy (ABS 2011). Horticulture (fruit and vegetables) and livestock production are also very important to the region's economy and its communities. Industries have made important gains in recent years towards minimising their off-farm impacts on the environment, but further improvements are required if the Reef Plan's water quality goals are to be realised (Brodie et al. 2008). In its synthesis of the available evidence, the Reef Scientific Taskforce concluded there is now considerable evidence to link areas of intensive agricultural production (particularly sugarcane) in the region to the presence in groundwater of pesticide residues and elevated nitrate levels (Brodie et al. 2008). The Taskforce highlighted the need to better understand and quantify the groundwater transport of these contaminants to the Reef lagoon.

This study was commissioned by the Queensland Government as part of its Reef Protection Program, to complement regulations introduced under the *Great Barrier Reef Protection Amendment Act 2009*. The Reef Protection Program is tasked with reducing, through improved on-farm management, the off-farm transport to the Reef lagoon of contaminants from cane-growing areas in the Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas (Figs. 1.1–1.3), as well as from grazing areas. Of most relevance to groundwater are nutrients and herbicides from cane-growing in these areas, but the review also includes issues concerning horticulture, where information is available. Note that in Figs. 1.1–1.3, aquifer boundaries may not necessarily align closely with respective catchment boundaries.

The purpose of the study was to provide an up-to-date review and synthesis of current knowledge on groundwater flows of nutrients and herbicides to the Reef lagoon, and the processes that influence them. The review was guided by three priority needs:

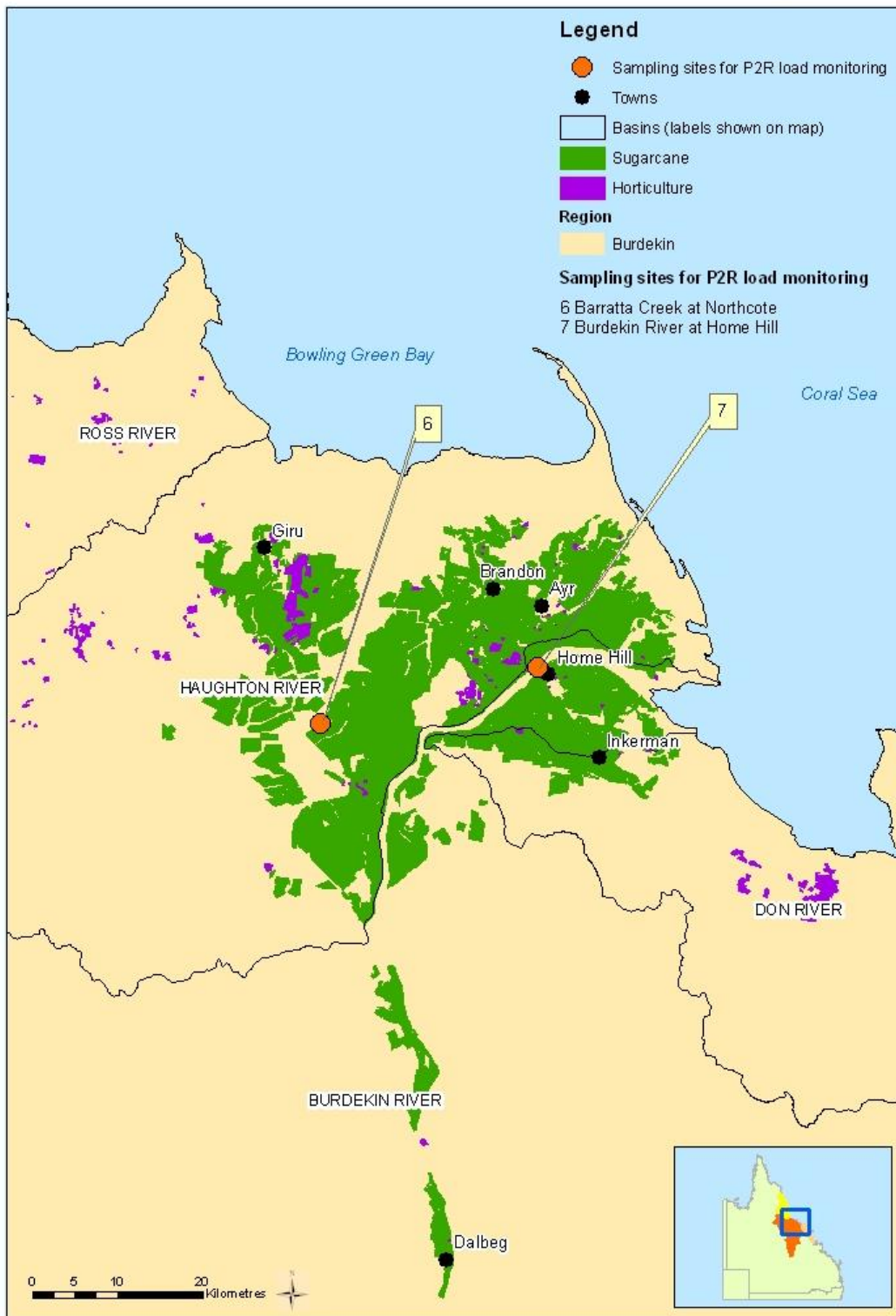
- i. Inform policy development, especially for future Reef Plan development, and identify critical knowledge gaps that currently limit our understanding of the problem and our ability to implement effective mitigation and monitoring strategies
- ii. Advise growers and others on management options for on-farm mitigation

- iii. Ensure Paddock-to-Reef scale monitoring, modelling and reporting programs take adequate account of groundwater discharges of these constituents.



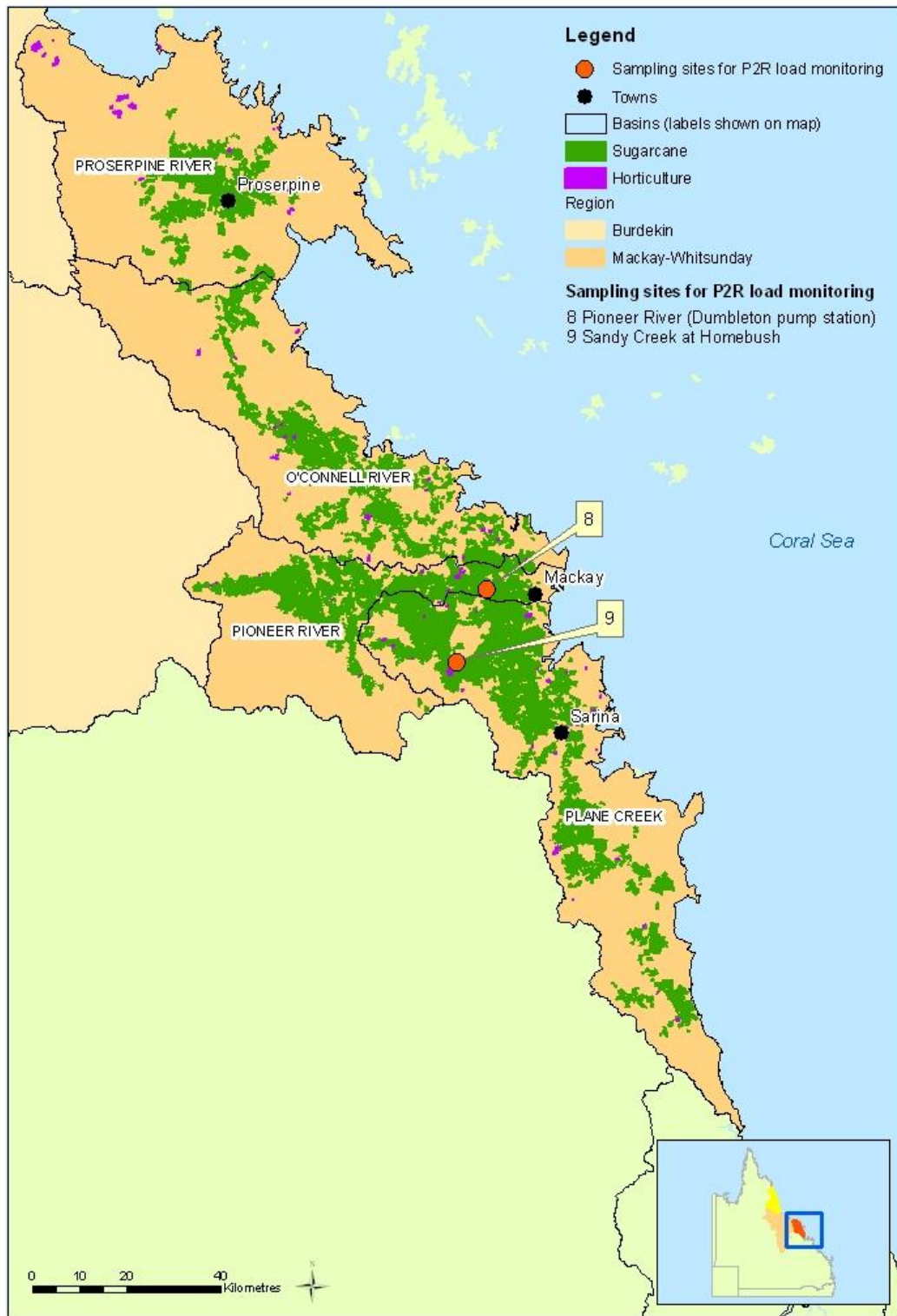
The 2009 land use data shown is a product of the Queensland Land Use Mapping Program (QLUMP). It was prepared as part of a land use change mapping project in the GBR catchments (funded by the Queensland Government Reef Protection R&D portfolio).

Figure 1.1. Sugarcane and horticulture land use in the Wet Tropics area and locations of the Paddock-to-Reef program’s end-of-system and sub-catchment monitoring sites.



The 2009 land use data shown is a product of the Queensland Land Use Mapping Program (QLUMP). It was prepared as part of a land use change mapping project in the GBR catchments (funded by the Queensland Government Reef Protection R&D portfolio).

Figure 1.2. Sugarcane and horticulture land use in the lower Burdekin and Don areas, and locations of the Paddock-to-Reef program’s end-of-system monitoring sites.



The 2009 land use data shown is a product of the Queensland Land Use Mapping Program (QLUMP). It was prepared as part of a land use change mapping project in the GBR catchments (funded by the Queensland Government Reef Protection R&D portfolio).

Figure 1.3. Sugarcane and horticulture land use in the Mackay–Whitsunday area and locations of the Paddock-to-Reef program’s end-of-system monitoring sites.

1.2 Nutrients and herbicides

The specific focus of the review was on groundwater processes and fluxes of nitrogen (N), phosphorus (P), and those herbicides that impair photosynthesis by disrupting Photosystem II (PSII) processes of target (and non-target) plants. These herbicides are referred to hereafter as ‘PSII herbicides’. The priority given to these contaminants was guided by the Reef Plan’s objectives and targets (The State of Queensland 2009a), backed by conclusions of the Reef Scientific Taskforce (Brodie et al. 2008) and an assessment of relative risks to the Reef from broad-scale agriculture (Brodie and Waterhouse 2009). Note that the term ‘contaminant’ where used in the report indicates the presence of substances at concentrations above background levels, but without specific reference to any adverse ecological effects such concentrations may (or may not) cause (Chapman 2007). It is possible that in some instances the Reef may also be at risk from the presence of other contaminants (e.g., heavy metals) but discussion of these was outside the scope of the review.

Both N and P are essential nutrients for all forms of life. They occur naturally in the environment in various forms, with microbial processes often mediating the conversion from one form to another (discussed later in the report). Both nutrients are widely applied to sugarcane crops to boost yields (e.g., in the form of manufactured fertilisers or organic amendments), with legume crops sometimes grown to increase soil N levels. Degradation of N and P compounds does not reduce the total amount of N and P present in the environment as a whole, rather it alters the forms and/or the environmental compartment(s) in which they occur (e.g., in the case of N, soil vs. atmosphere). Thus, a holistic approach is needed when assessing the mitigation potential of alternative management practices, to ensure that the problem is not merely shifted from one part of the environment to another.

The use of herbicides is an essential component of many modern farming systems, including sugarcane production. Commercially used herbicides are synthetic compounds that do not occur naturally in the environment. They are susceptible to degradation and are relatively short-lived, although in some cases degradation products may retain the herbicidal properties of the parent compound (discussed in later sections of the report). A variety of herbicides is used on cane in the Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas to control weeds during plant and ratoon crops and during fallow periods, with only minor differences across districts in the particular products used (C. Johnson, pers. comm.). Five of the chemicals commonly applied are PSII herbicides: ametryn, atrazine, diuron, hexazinone and metribuzin, although the use of diuron is currently suspended for certain high risk periods (under review).

The presence in surface waters of undesirable concentrations of PSII herbicides poses a threat to ecosystem health, including that of the Reef lagoon. Photosynthetic organisms such as mangroves, seagrasses and the symbiotic zooxanthellae of corals are susceptible to harm from these herbicides, with effects likely to range from temporary impairment of photosynthetic activity, to longer-term changes in community structure as a result of chronic exposure (Lewis et al. 2009). Similarly, excessive levels of N and P in surface waters can lead to a loss of biodiversity and a proliferation of undesirable species such as macroalgae (Fabricius 2005).

1.3 Outline of the review

Specific objectives of the study were to review and assess:

- Current knowledge of aquifers and groundwater processes across the study areas, including groundwater–surface water interactions, and spatial and temporal patterns of water level fluctuations and groundwater flows
- The occurrence of N, P and PSII herbicides in groundwater in the study areas
- Processes that underlie transformations and attenuation of these contaminants in the root zone and deeper subsurface environments, their transport to the Reef lagoon, and the links to on-farm management

- The relative importance of groundwater flows of N, P and PSII herbicides to the Reef lagoon from the study areas, relative to surface water flows
- The need for enhancement of current Paddock-to-Reef (P2R) monitoring (and modelling) programs to take account of nutrient and herbicide loads transported via groundwater pathways
- Critical knowledge gaps that need to be addressed so that effective mitigation and monitoring strategies can be devised and implemented.

Information assessed in the review was sourced primarily from the published literature, from unpublished material, and from discussions with key specialists from the scientific, natural resource management, policy and planning fields. The review and report were structured around four broad, inter-related themes:

- i. Aquifers and groundwater processes
- ii. Nutrients and herbicides in groundwater
- iii. Processes affecting N, P and PSII herbicides in the root zone and deeper subsurface environments, and the links to on-farm management
- iv. Groundwater fluxes of nutrients and herbicides to the Reef lagoon.

The report identifies and discusses key processes within each theme, at scales ranging from detailed molecular reactions (e.g., within the root zone and aquifer sediments), to much broader-scale processes, e.g., groundwater flows from aquifers to the Reef lagoon. It was not an exhaustive review covering all facets of every topic. Rather, the report presents an overview to a level of detail sufficient to give a scientifically credible assessment across the breadth of topics, themes and areas that can inform future policy-making, planning and research direction. Note that a glossary of technical terms used in the report is provided in Appendix 3.

Synthesis of the information in the report includes an overall assessment of current knowledge (and gaps) concerning the links between source areas of nutrients and PSII herbicides, their movement to groundwater, and their transformation, attenuation and transport to the Reef lagoon. It evaluates the relative importance of groundwater vs. surface water flows of these contaminants to the Reef lagoon and the links to on-farm management. Assessment is also made of the need for enhancement of current Paddock-to-Reef monitoring programs so they adequately account for loads of nutrients and PSII herbicides transported by groundwater to the Reef lagoon.

A set of fourteen conceptual models was developed in conjunction with the review to highlight and summarise important aspects of the transport, transformation and attenuation of N, P and PSII herbicides in the root zone and deeper subsurface environments. Collectively, the conceptual models integrate key processes and pathways, from farm scale to the Reef (Fig. 1.4). Conceptual models of root zone processes and of those in deeper subsurface layers are accompanied by a 'depth locator' to indicate the specific soil or sediment layers described (Fig. 1.5). Note that hereafter, unless stated otherwise the term 'subsurface' refers to depths beneath the root zone. A full set of these conceptual models is available for download from www.reefwisefarming.qld.gov.au/.

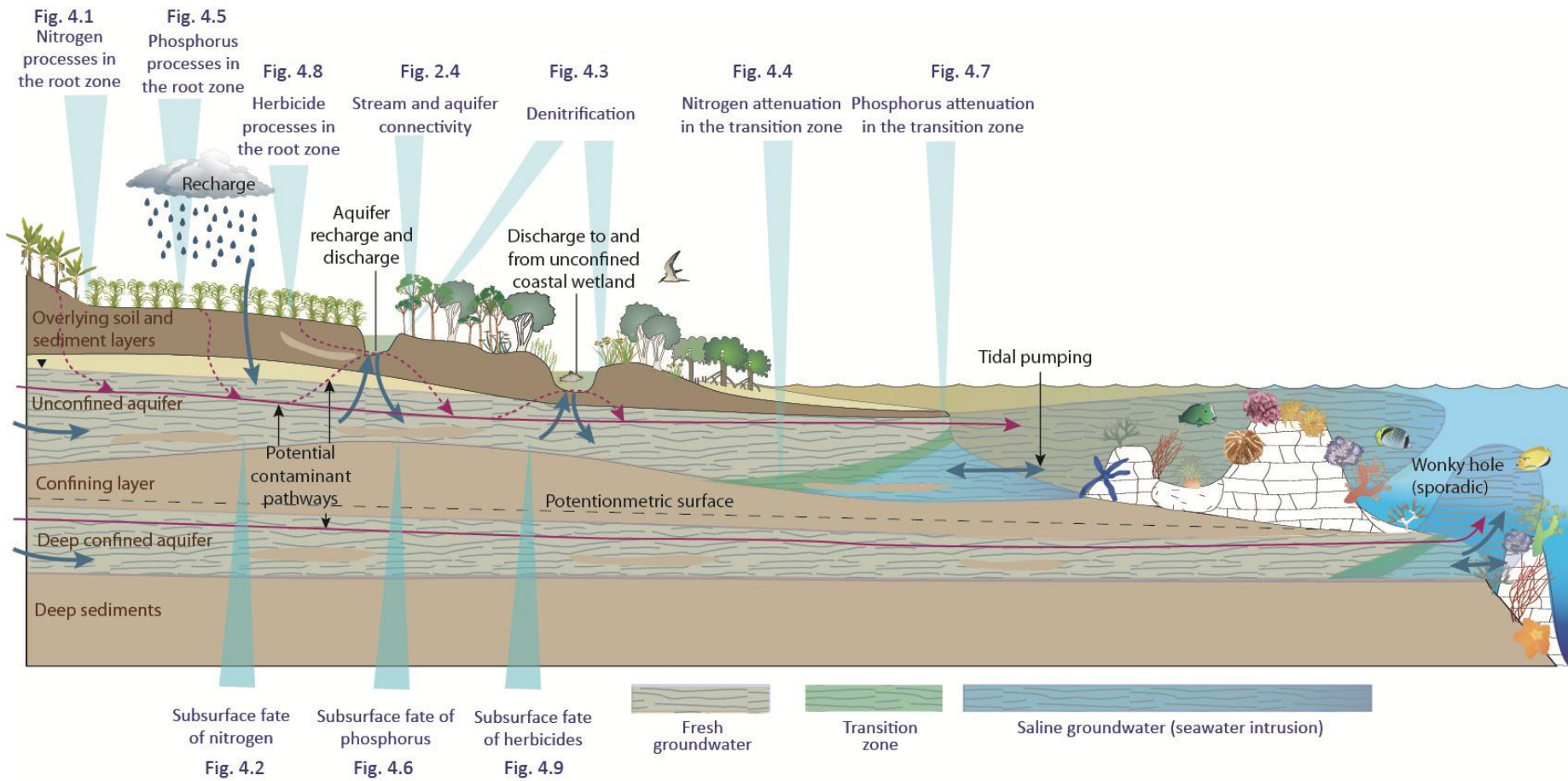


Figure 1.4. Overview of key processes summarised in conceptual models in the report, and their collective role in describing potential groundwater flows of nutrients and herbicides to the Reef lagoon. Each conceptual model is identified by its figure number in the report.

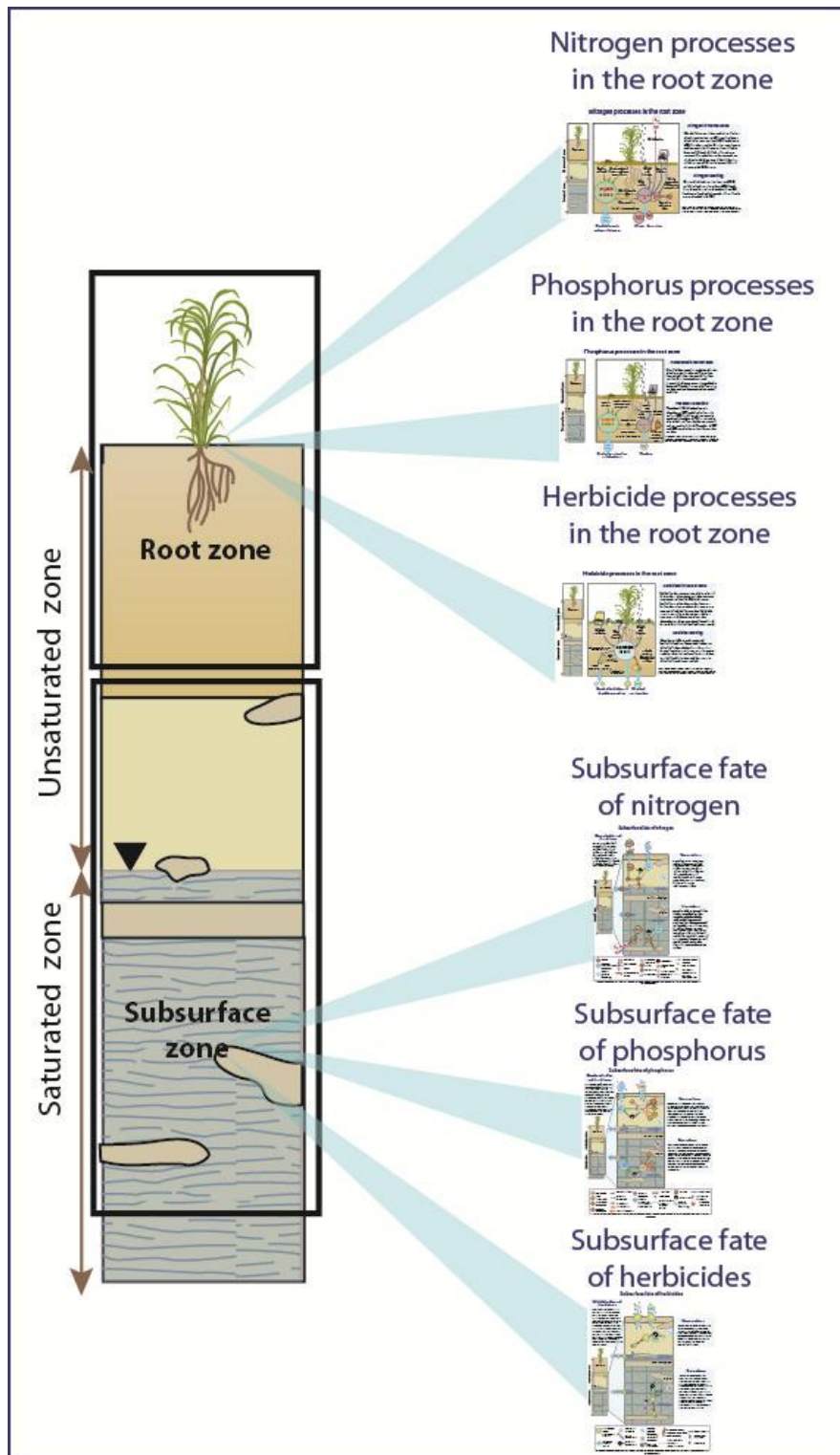


Figure 1.5. The 'Depth locator', which is positioned to the left of each conceptual model of root zone and deeper subsurface zone processes to indicate the specific soil and sediment layers described.

2. Regional Aquifers and Groundwater Processes

2.1 Regional aquifers

There is considerable diversity of aquifer size, complexity and groundwater–surface water connectivity across the Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas. Climatic conditions across these areas vary widely. Sugarcane is the major, or a significant crop, even though the conditions under which it's grown differ considerably across the three areas, including the extent of crop irrigation. Details for each of the main aquifer systems within the study areas are provided in Appendix 1 (Tables A1.1–A1.3). The Don is included in Table A1.2 as it is an important horticultural area that relies on groundwater for irrigation and town supply.

Unconfined alluvial aquifers are widely represented across the study areas and are variously composed of silt, mud, clay, sand and gravel (Tables A1.1–A1.3). Confined or semi-confined portions of alluvial aquifers are present in some systems (e.g., in the lower Herbert and lower Burdekin) while fractured bedrock aquifers also occur. In some systems individual layers of the alluvium appear inter-connected and behave hydraulically as a single unit despite some inherent differences (e.g., the lower Burdekin, Fig. 2.1; and the Pioneer Valley, Fig. 2.2) while others exhibit a more complex structure and behaviour (e.g., the lower Herbert, Fig. 2.3). All systems show dynamic connectivity between groundwater and streams.

2.2 Surface water–groundwater connectivity

Overview

Groundwater and surface water interact at many points throughout the landscape as groundwater moves through aquifers from areas of recharge to areas of discharge. The interface between the two water bodies at these points provides a dynamic environment that supports a variety of aquatic ecosystems (Winter et al. 1998). The hydraulic conductivity of an aquifer has a major influence on groundwater flow, with water flowing from the point of highest hydraulic head to the lowest. The former point is often defined by surface topography (or outcrop of aquifer sediments) while the latter typically occurs in conjunction with a wetland, stream or marine water body (Reid et al. 2009). Groundwater flow paths in shallow, unconfined aquifers can be relatively short (e.g., around 100 m or less) with residence times of days to a few years; while flow paths in deep aquifers may be much longer (many kilometres), with corresponding residence times of decades to centuries or more.

Groundwater recharge occurs when water infiltrates through overlying soil and sediment layers to an aquifer. This typically occurs directly via percolation of rainfall, or as seepage from a streambed when the water level in the stream is above the level of the watertable (a losing stream, Fig. 2.4) (Winter et al. 1998). In some instances aquifers can be artificially recharged; e.g., as occurs via recharge channels and pits in the Burdekin Delta to reduce the risk of seawater intrusion (McMahon et al. 2012).

Groundwater discharge to streams occurs when the watertable in the adjacent aquifer is higher than that of the associated stream (a gaining stream, Fig. 2.4) (Winter et al. 1998). Streams can have both gaining and losing reaches and the direction of flow may reverse seasonally. Discharge of shallow groundwater through streams traversing the alluvia is a feature of many areas, e.g., the Pioneer Valley, the lower Herbert, the Tully–Murray and the Mulgrave–Russell (Tables A1.1–A1.3). Artificial drainage networks have been constructed in some parts of these areas to reduce watertable levels and thereby prevent waterlogging of cane crops (Tables A1.1–A1.3).

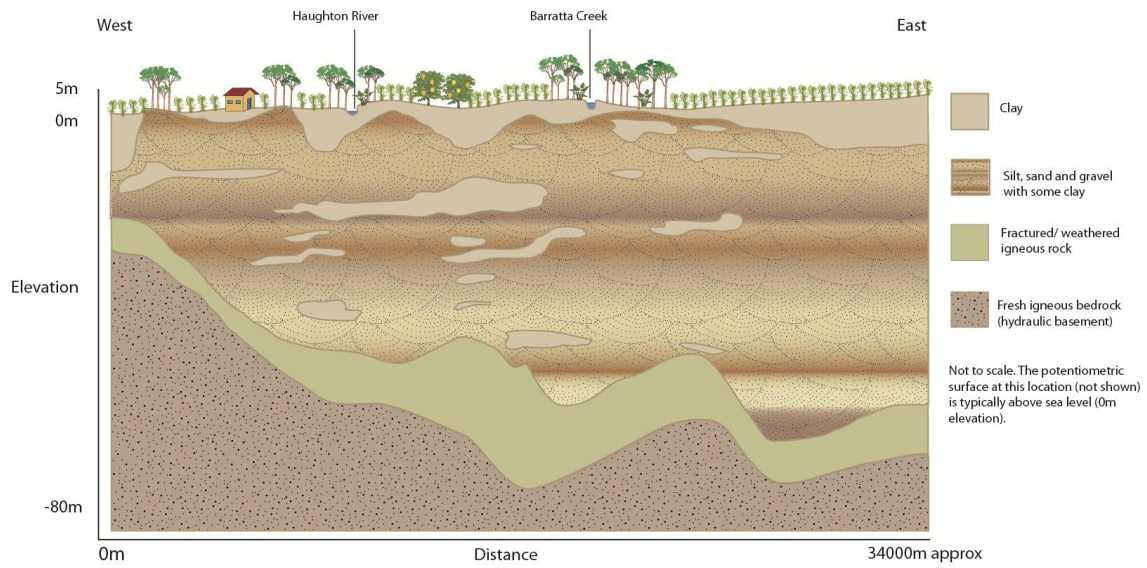


Figure 2.1. Conceptualisation of a cross-section of the lower Burdekin aquifer, near Giru. Adapted from McMahon et al. (2012), with minor modification.¹

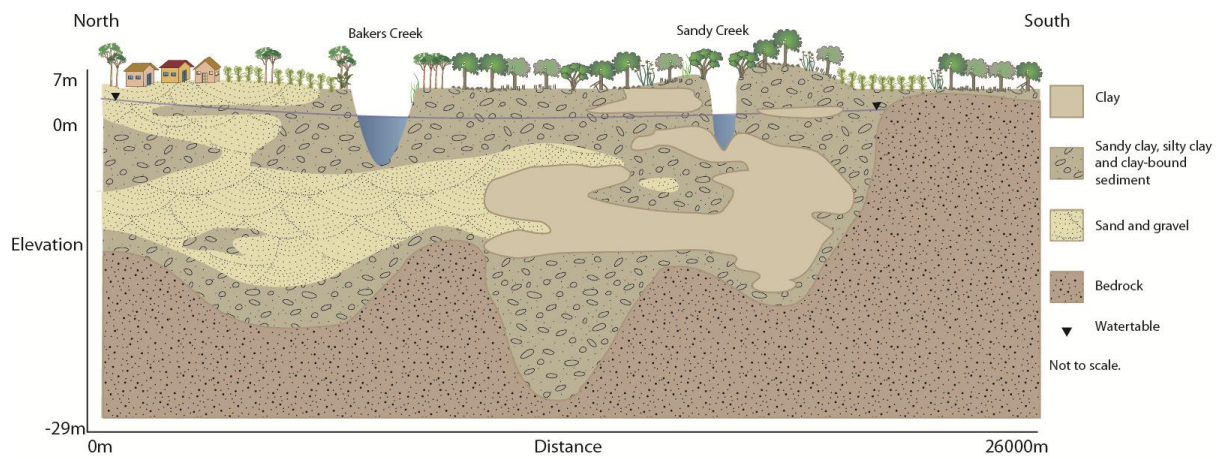


Figure 2.2. Conceptualisation of a cross-section of the Pioneer Valley aquifer at the coastal outflow. Adapted from Murphy et al. (2005).

¹ Modified on the advice of G. McMahon (pers. comm.).

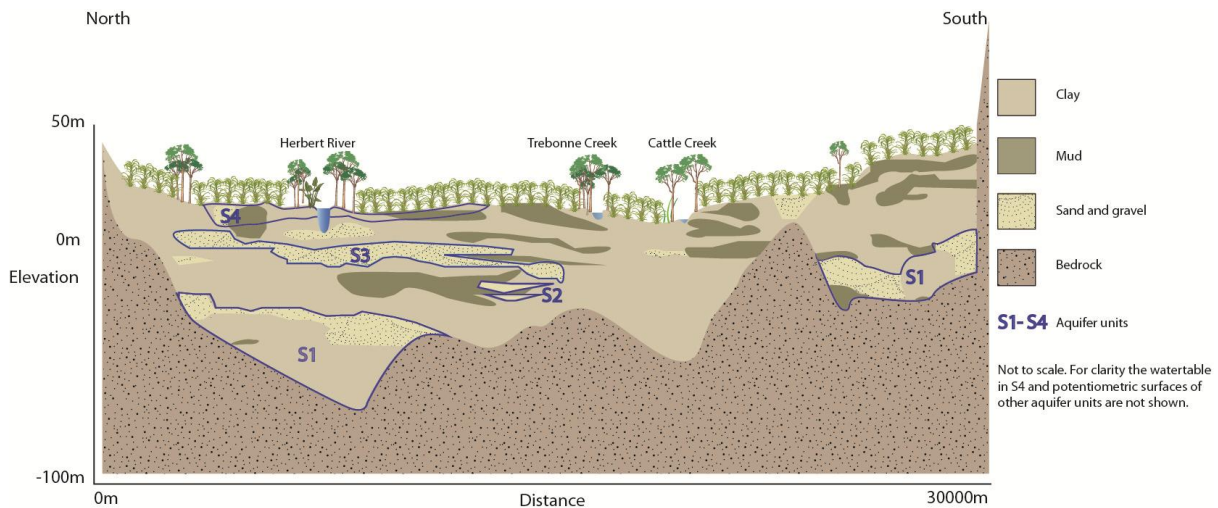


Figure 2.3. Conceptualisation of a cross-section of the lower Herbert aquifer, near Ingham. Adapted from DSITIA (2012d).

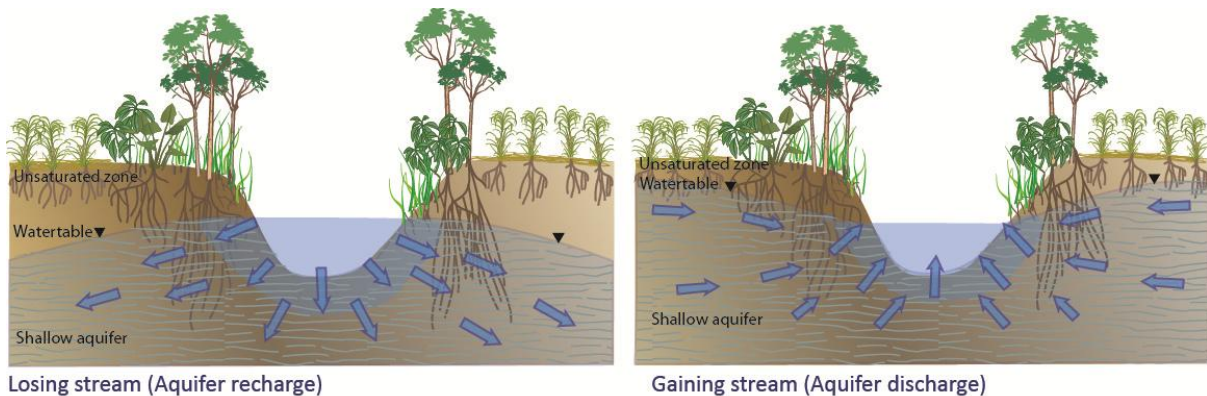


Figure 2.4. Conceptualisation of stream and aquifer connectivity, showing aquifer recharge (losing stream) and discharge (gaining stream). Adapted from Winter et al. (1998).

Watertables rise when the rate of recharge to an aquifer exceeds its capacity to transmit excess water to points of discharge. Seasonal fluctuations in watertable levels are a common feature of aquifers across the study areas, with large and rapid rises typically occurring in response to rainfall (Tables A1.1–A1.3). For example, in the unconfined aquifer of the lower Herbert (S4 unit, Fig. 2.3), groundwater levels fluctuate seasonally between around 1.5 m and 3 m depth (Cox 1979, cited by DSITIA 2012d), while in the lower Burdekin, large rainfall events can increase groundwater levels by up to 5 m in the unconfined aquifer in the Burdekin Delta, and by around 1 m in the semi-confined aquifer (McMahon et al. 2012). Similarly, in the lower Johnstone, large and rapid water level rises in response to rainfall are observed in some bores, in some cases followed by rapid recession as groundwater discharges to streams (DSITIA 2011b).

An overall trend of rising groundwater levels in parts of the lower Burdekin is now recognised to be of serious concern for the viability of future cropping in affected areas, with increases in root-zone salinity a major issue (Bennett 2012). Considerable efforts are now being made to address the problem and assess the options for mitigation, including the likely benefits of improved water use efficiency in the irrigation management of cane (Bennett 2012). Other aquifers within the study areas that show probable trends for rising water levels over time include those in the Barron Delta, lower Johnstone, Don, Proserpine and Pioneer Valley (McNeil and Raymond 2011). Rising groundwater levels not only increase risks of contamination from anthropogenic sources as water levels rise close

to the land surface (Winter et al. 1998), they also increase the likelihood of the contaminated groundwater being discharged to riverine and coastal receiving environments. There are also risks that groundwater-dependent ecosystems may perish as groundwater levels rise: e.g., aerated root zones of riparian vegetation may become waterlogged and anaerobic, resulting in a succession to a new plant community of wetland species (Dillon et al. 2009).

Temporary storage of stream water in stream banks (bank storage) or as perched watertables within riparian areas are two further forms of surface water–groundwater interaction. These occur during runoff events when rising stream waters move into stream banks or riparian zones, and then drain back to the stream as stream waters recede (Rassam et al. 2008). These processes are not considered further in this review since they arise from surface flow processes (and associated links to land management) rather than via deep drainage.

Groundwater–seawater interface

The coastal interface between groundwater and seawater is not a sharp boundary but rather a transition zone, the nature of which is determined by factors such as the hydrogeology of the aquifer, hydraulic gradients, tidal fluctuations, climatic stresses, and the nature of coastal features and estuaries (Fetter 1994, cited by Werner et al. 2005). At a localised scale, groundwater pumping can also alter the nature of the transition zone by increasing dispersion and creating ‘upconing’ effects (G. McMahon, pers. comm.). Typically, low salinity groundwater overlies seawater in the interface zone. The overlying fresh groundwater may discharge to the coast at or near the shoreline, or further offshore, if buried paleochannels are present (discussed below).

Seawater can intrude significantly into coastal aquifers and impair groundwater quality in production bores when groundwater levels become too low, e.g., following extended periods of low rainfall and over-extraction. Within the study areas, the Pioneer Valley and the Burdekin Delta are recognised as experiencing significant impact from seawater intrusion (Werner et al. 2008, Werner 2010). The Burdekin Delta is a complex mosaic of inter-bedded mud, silt, clay, sand and gravel layers which presents challenges in defining the interface zone and managing groundwater levels to minimise seawater intrusion (McMahon et al. 2001). The position of the interface can vary seasonally and in the north Burdekin area, the ‘toe’ extends many kilometres inland (McMahon et al. 2001).

Submarine groundwater discharge

Over the past 20 years there has been increasing awareness of the importance of submarine groundwater discharge (SGD) as a potential pathway for groundwater contaminants to directly enter coastal waters and ecosystems. SGD is defined by Burnett et al. (2003) as ‘any and all flows on continental margins from the seabed to the coastal ocean, regardless of fluid composition or driving force’. It encompasses a variety of processes involving groundwater flow from land, as well as seawater flow through sediments, including the following (Stieglitz 2005, Fig. 2.5):

- i. SGD from unconfined coastal aquifers, in the form of diffuse seepage in the near-shore zone
- ii. SGD from confined or semi-confined coastal aquifers, as discrete springs in the near-shore zone
- iii. SGD from confined submarine aquifers (associated with buried paleochannels of riverine/estuarine origins), through ‘Wonky Holes’ further off-shore (Stieglitz and Ridd 2000).

Related processes include seawater recirculation through crustacean burrows (e.g., in mangrove forests) (Stieglitz 2005); wave and tide-induced flow oscillations (Li et al. 1999, Carey et al. 2009); and seasonal inflow and outflow of seawater into the aquifer (Burnett et al. 2006).

SGD is considered a ubiquitous process. Flow rates are typically low and discharge is diffuse, widespread and spatially and temporally patchy, which makes quantification of fluxes difficult (Burnett et al. 2003, 2006). However, it is considered that reliable estimates can be obtained, particularly when made using multiple methods over time periods that take account of spatial and

temporal variability (Burnett et al. 2006). Globally, estimates of terrestrially-derived ‘fresh’ SGD (i.e., not from re-circulation processes) suggest they are typically $\leq 10\%$ of surface water inputs, which while not large in those terms is considered important, particularly concerning the potential threats to coastal ecosystems from any contaminants discharged (Burnett et al. 2003).

Several studies over the past twelve years have investigated the occurrence of SGD in the GBR region (e.g., Stieglitz 2005, Stieglitz et al. 2010, Cook et al. 2004, 2011). These have involved the use of a naturally occurring radon isotope (^{222}Rn) which is an ideal tracer since levels tend to be enriched in groundwater compared with surface water and it is relatively short-lived. Isotopes of radium have also been used. A seismic survey of northern and central Halifax Bay (offshore from the Herbert River catchment, Fig. 1.1) revealed the presence of approx. 100 Wonky Holes at a depth of around 20 m below the surface, ranging from 10–30 m in diameter and up to 4 m deep (Stieglitz and Ridd 2000). Detailed salinity and conductivity measurements suggested the possibility of fresh groundwater discharge from these holes. Further investigations showed similar depressions offshore from several other rivers in the Wet Tropics (e.g., the Daintree R. and the Barron R.), up to 10 km from the coast (Stieglitz and Ridd 2003).

Radiochemical studies using ^{222}Rn coupled with geophysical measurements have since shown SGD to occur in the study areas in a variety of forms and settings, from the inter-tidal zone to the inner shelf (Stieglitz 2005). Two regional-scale surveys provided further qualitative insights into SGD processes, through continuous recording of ^{222}Rn and salinity along 300 km transects, approx. 1.8 km from the coast of the Wet Tropics; while a separate study in Bowling Green Bay in the Burdekin (Fig. 1.2) assessed SGD processes over a range of seasonal conditions (Stieglitz et al. 2010). Maps of ^{222}Rn transects along the coast revealed the occurrence of SGD processes at many locations, including in riverine fluxes (e.g., from the Johnstone R. and Tully R.), terrestrially-derived fresh SGD (e.g., offshore from areas to the south of the Johnstone River system) and tidal pumping of seawater through mangrove forests (e.g., in the Hinchinbrook Channel).



Figure 2.5. Examples of submarine groundwater discharge in the Wet Tropics, at Ella Bay (top) and Elim Beach (bottom). From Stieglitz (2005), reproduced with permission, Elsevier Ltd.

Two detailed studies conducted in Bowling Green Bay provided quantitative estimates of groundwater discharge from the lower Burdekin aquifer into the Bay, using ^{222}Rn and radium isotope tracers in a mass-balance approach (Cook et al. 2004, 2011). This included making allowance for the flux of recirculated seawater, which was a significant source of uncertainty in the estimates. Groundwater fluxes directly into Bowling Green Bay were similar in both sampling periods, and when extrapolated from daily ^{222}Rn measurements made at the end of the 2011 wet season, were in the range of approx. 31,000–157,000 ML/y. In May 2011, the daily groundwater flux to Bowling Green Bay of 86–430 ML/d (based on ^{222}Rn measurements) can be compared with river discharge to the bay at that time of 1300 ML/d, while in the 2004 study, river discharge was much lower and the daily groundwater flux to the bay exceeded the flux from the river at that time. Groundwater fluxes from the lower Burdekin aquifer in these studies were measured at the end of respective wet seasons so the estimates are probably at the high end of the range seasonally (Cook et al. 2011).

Groundwater discharge to streams

Groundwater discharge from several rivers and streams in the lower Burdekin was quantified through detailed monitoring of ^{222}Rn levels and electrical conductivity in stream waters, in conjunction with the two studies above (Cook et al. 2004, 2011). Groundwater discharge to streams was less in May 2004 than in May 2011 and varied seasonally, being highest at the end of the wet season. In 2011, daily groundwater discharge was measured along stream lengths of 62 km, 52 km and 60 km from the mouths of the Burdekin River, Haughton River and Barratta Creek, respectively: discharge rates were 248 ML/d (Burdekin R.), 138 ML/d (Haughton R.), and 56 ML/d (Barratta Ck.) (Cook et al. 2011). In each case, groundwater discharge was unevenly distributed along the stream length. Groundwater discharge to Bowling Green Bay at that time was estimated to be 260 ML/d (mid-range estimate), giving a total groundwater daily flux from the lower Burdekin aquifer to the Bay of 700 ML/d (Cook et al. 2011). However, there is considerable uncertainty associated with these estimates; e.g., in the case of river estimates it is likely to be well in excess of $\pm 50\%$ (Cook et al. 2011). Similar studies to quantify groundwater discharge to rivers and streams (or the coast) at this scale and level of detail have not been conducted elsewhere in the GBR region.

A study conducted in the lower Herbert floodplain found differing responses to rainfall in a semi-confined aquifer and a shallower perched watertable that was present throughout the nineteen month study (Pearce and Bohl 2004). While the perched watertable responded rapidly to rainfall, it did not show a similar rise of around 1 m, as occurred in the deeper aquifer after a prolonged period of rain. This was attributed to the efficiency of the surface drainage network in rapidly draining the shallow perched groundwater. Shallow watertables are a common feature of cane-growing areas in the lower Herbert floodplain, with approx. 15,000 ha of cane being prone to waterlogging (Mitchell 2005).

Modelled estimates of groundwater discharge

The Water Planning Sciences group of the Department of Science, Information Technology, Innovation and the Arts (DSITIA) is developing groundwater flow models to support ongoing development of Water Resource Plans for major Queensland catchments. The group now has draft groundwater model conceptualisation reports for six groundwater systems across the three GBR areas that are within the scope of this review: lower Russell-Mulgrave (DSITIA 2011a); lower Johnstone (DSITIA 2011b); lower Tully-Murray (DSITIA 2011c); lower Herbert (DSITIA 2012d); lower Burdekin (McMahon et al. 2012); and the Pioneer Valley (Murphy et al. 2005). Draft water balance estimates presented for each groundwater system include estimates of both recharge and discharge, with the latter defining groundwater discharge to rivers, streams and drains, as well as to the coast. Water balance estimates for the lower Burdekin (McMahon et al. 2012) are an exception, in which data for groundwater discharge via rivers, streams and drains are not available, since only net groundwater recharge data were presented in the water balance. Mean annual discharge estimates in Table 2.1 were derived from water balance calculations based on long-term data records (see Glossary).

Table 2.1. Draft water balance estimates of long-term mean annual groundwater discharges from six lower floodplain aquifers and comparisons with mean annual stream-flows

Aquifer	GW discharge to rivers, streams & drains	GW discharge directly to the coast	Total GW discharge to surface waters¹	Stream-flow²	Total GW discharge as a proportion of stream-flow
	(ML/y)	(ML/y)	(ML/y)	(ML/y)	(%)
Mulgrave–Russell ³	99,300 ⁴	Not available	Not available	4,193,000	2.4
Johnstone ⁵	289,616	2,726	292,342	4,698,000	6.2
Tully–Murray ⁶	334,448	720	335,168	5,311,000	7.1
Herbert ⁷	474,583	550	475,133	4,991,000	9.5
Burdekin ⁸	161,400 ⁹ (Not available)	94,965 (12,231)	256,365 (Not available)	10,100,000	2.5
Pioneer ¹⁰	21,553 ¹¹	15,687	37,240	994,000 ¹²	3.8

¹Sum of two previous columns; ²Hausler (1991); ³GW data from DSITIA (2012a); ⁴Average for two different irrigation scenarios; ⁵GW data from DSITIA (2012b); ⁶GW data from DSITIA (2012c); ⁷GW data from DSITIA (2012d); ⁸Note, GW data were not derived from water balance but extrapolated from May 2011 daily estimates in Table 5.1 of Cook et al. (2011); water balance estimates of McMahon et al. (2012) are shown in brackets below, where available; ⁹Includes Burdekin R., Haughton R. and Barratta Ck. (from Cook et al. 2011); ¹⁰GW data from Murphy et al. (2005); ¹¹Includes Pioneer R., Bakers Ck., Sandy Ck., Alligator Ck., Bell Ck., Splitters Ck.; ¹²Pioneer R. only.

Despite the inherent uncertainties associated with the groundwater discharge estimates in Table 2.1, some broad comparisons can be made. In all cases, mean annual total groundwater discharge is <10% of mean annual stream-flow (Table 2.1). Furthermore, in the Wet Tropics, groundwater discharge to rivers, streams and drains far outweighs (by orders of magnitude) that discharged directly to the coast, but this is not the case for the Pioneer or the lower Burdekin. Based on these estimates, annual groundwater discharge directly to the coast is greatest from the lower Burdekin aquifer >>>Pioneer Valley >>lower Johnstone >lower Tully–Murray and lower Herbert (noting that data on groundwater discharge to the coast from the Mulgrave–Russell aquifer were not available) (Table 2.1). In the lower Mulgrave–Russell, around 95% of the total groundwater discharge to rivers, streams and drains is accounted for by discharge through drains (DSITIA 2011a).

It should also be noted that Cook et al.’s (2011) estimate of annual groundwater discharge from the lower Burdekin aquifer to the coast was based on measurements made in May 2011 (at the end of the wet season) and was almost eight times the mean annual estimate derived by McMahon et al. (2012) (Table 2.1). Furthermore, the former study quantified groundwater discharge from the aquifer northwards to Bowling Green Bay, but not eastwards directly to the Coral Sea, while the latter included discharge to both coasts (Fig. 1.2). Groundwater discharge eastwards to the Coral Sea was previously estimated to be in the range 1,500–9,000 ML/y (McMahon et al. 2002, cited by McMahon et al. 2012). Differences between these two sets of estimates for the lower Burdekin may in part be due to the much higher groundwater levels at the time of Cook et al.’s (2011) measurements, compared with the long-term mean levels (1981–2006) that were used by McMahon et al. (2012).

2.3 Summary of key points

- Unconfined alluvial aquifers are widely represented across the Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas, with confined or semi-confined aquifers also present in some areas; there is a high degree of connectivity between groundwater and surface waters in all three areas
- Marked seasonal fluctuations in groundwater levels are common, but longer-term trends for rising groundwater levels are evident in some aquifers, particularly in parts of the lower Burdekin
- Overall, the estimated mean annual groundwater discharge from each of the main aquifers is <10% of mean annual discharge from the corresponding river system
- Groundwater discharge to rivers, streams, wetlands and drains in the Wet Tropics far exceeds groundwater discharge directly to the coast from aquifers in that area
- By contrast, groundwater discharge directly to the coast in the lower Burdekin and Mackay–Whitsunday areas represents around 40% of respective total groundwater discharge from each aquifer (i.e., in both cases, groundwater discharge to the coast is of similar proportions to that to rivers)
- Shallow groundwater is discharged through streams in many parts of the Mackay – Whitsunday and Wet Tropics areas, with artificial drainage networks constructed in low-lying areas to reduce watertable levels rapidly and so minimise waterlogging of crops
- Submarine groundwater discharge (SGD) directly to the coast has been identified and mapped at numerous locations along the Wet Tropics coast and in Bowling Green Bay (in the lower Burdekin) but has been quantified only in Bowling Green Bay; SGD has not been mapped in the Mackay–Whitsunday area
- Similarly, groundwater discharge to rivers and streams has been quantified at the end of the wet season in the lower Burdekin, but has not been quantified for any parts of the Wet Tropics and Mackay–Whitsunday areas.

3. Nutrients and Herbicides in Groundwater

3.1 Introduction

The section reviews the reported presence in groundwater of the various forms of N and P, and the suite of PSII herbicides (and their breakdown products) most commonly used for sugarcane production. Several other groundwater constituents or properties can influence the fate of these contaminants in subsurface environments, e.g., dissolved organic carbon (DOC), dissolved oxygen (DO), oxidation-reduction potential (Eh, also known as redox potential), pH, and reduced forms of manganese, iron and sulfur. However other than DOC, concentrations of these constituents were reported in few of the studies reviewed, so they are referred to where relevant in the following section on contaminant attenuation (Section 4), with only DOC discussed further here.

The biogeochemistry of uncontaminated groundwater is strongly influenced by the geology of the aquifer materials that are present and by the duration of contact. Processes involved include acid-base reactions, precipitation/dissolution of minerals, sorption and ion exchange, oxidation/reduction, biodegradation and dissolution/exsolution (Winter et al. 1998). Nitrate can be present in uncontaminated groundwater in certain situations (Bolger et al. 1999), as can ammonium (Schilling 2002) and P (Ruttenberg 2001). As noted previously, the PSII herbicides used in the cane industry are synthetic products that do not occur naturally in the environment. The risk of contamination as a result of land use and land management practices is generally considered to be greater for shallow aquifers than for those at depth (Winter et al. 1998), although nitrate contamination at depths >50 m has been reported in some Australian aquifers (Bolger et al. 1999).

Regional groundwater quality has been evaluated by DSITIA in its periodic assessments for the long-term state-wide monitoring and reporting program. However, the Queensland Government's groundwater database (GWDB) contains few pesticide or nutrient data except for nitrate. Several relatively short-term monitoring campaigns conducted in the study areas since 1990 have provided more detailed information on nutrients and herbicides in groundwater, although the range of analytes reported in these studies has varied. It is noteworthy that most of these surveys occurred more than 10 years ago and few studies included sites in the Wet Tropics. Note also, that differences between these various studies (e.g., in site locations, sample numbers and sampling frequencies) limit the extent to which detailed comparisons can be made between results.

3.2 Water quality guidelines

As noted previously, excessive levels of N and P in surface waters can lead to a loss of biodiversity and a proliferation of undesirable species such as macroalgae (Fabricius 2005). Similarly, the presence of undesirable concentrations of PSII herbicides can impair photosynthetic activity in susceptible organisms, with chronic exposure potentially having long-term effects on ecosystem health (Lewis et al. 2009). The Australian Water Quality Guidelines recommend concentrations (termed 'trigger values') for protecting aquatic ecosystems in tropical waters, including trigger values for various forms of N and P in lowland rivers, wetlands, estuaries and inshore marine waters (Table 3.1, ANZECC & ARMICANZ 2000). As discussed in Section 2.2 (and later in Section 5.4), groundwater is discharged to many of these environments in the Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas, which highlights the potential threats to them from contaminants contained in groundwater. It also emphasises the need for effective mitigation of contaminant loads prior to groundwater discharge, if natural attenuation is not sufficient (discussed in Chapter 4). The Australian Water Quality Guidelines similarly include trigger values for protection of freshwater and marine ecosystems from several PSII herbicides (ANZECC & ARMICANZ 2000, Table 3.2).

Currently, there are no contaminant trigger values for protecting subterranean ecosystems within aquifers, so the risks to them from nutrients and herbicides in groundwater cannot be assessed. As noted previously, groundwater is used in some areas for domestic purposes and for livestock watering.

The Australian Drinking Water Guidelines (ADWG) provide guideline values for protecting human health for a wide range of contaminants, including nitrate, nitrite and the PSII herbicides considered in this review (Table 3.3, NHMRC 2011). At present there are no specific guidelines for herbicides (or other pesticides) in livestock drinking water, so the ADWG are recommended to indicate safe levels for livestock consumption, as a precautionary measure (ANZECC & ARMCANZ 2000). Guidelines for nitrate and nitrite in livestock drinking water are given in Table 3.3².

Table 3.1. Trigger value concentrations (mg/L) for nutrients recommended by the Australian water quality guidelines for surface waters in tropical Australia^{1, 2, 3}

Ecosystem type	Total N	Oxidised-N ⁴	Ammonium-N	Total P	Filterable reactive P ⁵
Lowland river	0.20–0.30	0.010	0.01	0.01	0.004
Wetlands	0.35–1.2	0.010	0.01	0.01–0.05	0.005–0.025
Estuaries	0.25	0.030	0.015	0.02	0.005
Inshore marine	0.10	0.002–0.008	0.001–0.01	0.015	0.005

¹ANZECC & ARMCANZ 2000; ²Trigger values are concentrations below which there is a low risk that adverse ecological effects will occur, with follow-up investigation recommended if a trigger value is exceeded; ³Trigger values apply to protection of slightly disturbed ecosystems; ⁴(Nitrate + nitrite)-N; ⁵Consists of orthophosphate (PO₄³⁻) and other simple inorganic phosphates

Table 3.2. Trigger value concentrations of PSII herbicides recommended by the Australian water quality guidelines for protecting freshwater and marine species^{1, 2}

PSII herbicide	Trigger value (µg/L) ^{3, 4}	
	Freshwater	Marine
Atrazine	13 (M)	13 (L)
Hexazinone	75 (L)	75 (L)
Diuron	0.2 (L)	1.8 (L)

¹ANZECC & ARMCANZ 2000; ²Only those PSII herbicides used by the cane industry in the Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas are listed (note that trigger values are not yet available for ametryn and metribuzin); ³Reliability ratings are shown in brackets – (H) high, (M) moderate, (L) low; ⁴Note that a moderate rating provides protection of 95% of species while low rated trigger values should be used only as indicative interim working levels.

Table 3.3. Recommended guideline values for nitrate, nitrite and PSII herbicides in water for human consumption¹ and in drinking water for livestock²

Constituent ³	Guideline value (mg/L)	
	Human consumption	Livestock consumption ⁴
Ametryn	0.07	–
Atrazine	0.02	–
Diuron	0.02	–
Hexazinone	0.4	–
Metribuzin	0.07	–
Nitrate	50 ⁵	400 ⁶
Nitrite	3	30

¹NHMRC 2011; ²ANZECC & ARMCANZ 2000; ³Only those PSII herbicides used by the cane industry in the Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas are listed; ⁴No herbicide guidelines are available specifically for livestock consumption so those for human consumption are recommended as a precautionary measure; ⁵Up to 100 mg/L nitrate is safe for adults and children over 3 months; ⁶Stock may tolerate higher nitrate concentrations in drinking water provided concentrations in feed are not high; water containing >1500 mg/L nitrate is likely to be toxic to animals and should be avoided.

² Note: typically, for nitrate and nitrite, trigger values for ecosystem protection are expressed as concentrations of oxidised-N, i.e., the mass of N occurring as nitrate and/or nitrite (nitrate-N + nitrite-N); while guidelines for human and livestock health are based on the total masses of nitrate and nitrite, not simply their N contents.

3.3 Nitrogen

*Nitrate*³

Much more information has been published on nitrate in groundwater than on other forms of N (or on P or PSII herbicides). The review discusses ten studies that have focussed on groundwater nitrate concentrations in one or more of the three study areas since the mid-1990s (Table 3.4). Nitrite is a form of N that may occur naturally under certain conditions (e.g., low DO and Eh) but typically it is present only at low concentrations and is short-lived, being an intermediate in reactions involving the oxidation of ammonium and the reduction of nitrate (discussed in Section 4.1). Nitrite levels are of concern in groundwater used for human and livestock consumption (Table 3.3), since nitrite impairs the ability of haemoglobin to transport oxygen in the blood, particularly in infants. Only two of the studies listed in Table 3.4 specifically assessed nitrite levels in groundwater and in both cases, median concentrations were found to be very low (<0.002 mg nitrite-N/L) (Baskaran et al. 2001, 2002).

Table 3.4. Studies of nitrate in groundwater conducted in the three study areas since the mid-1990s

Study area	Specific areas	Reference
Wet Tropics	Johnstone	Hunter et al. (2001)
	Herbert, Tully, Johnstone, Mulgrave–Russell, Mossman	Thorburn et al. (2003)
	Herbert, Tully, Johnstone, Mulgrave, Barron Delta, Mossman	McNeil and Raymond (2011) ¹
Lower Burdekin and Don	Lower Burdekin	Budd et al. (2002)
	Lower Burdekin	Thorburn et al. (2003)
	Lower Burdekin	Barnes et al. (2005) ¹
	Lower Burdekin	Thayalakumaran et al. (2008)
	Lower Burdekin	McNeil and Raymond (2011) ^{1,2}
	Lower Burdekin	Lenahan (2012)
	Lower Burdekin	BBIFMAC (2012)
Mackay–Whitsunday	Don	Baskaran et al. (2001)
	Pioneer Valley	Baskaran et al. (2002)
	Pioneer Valley	Budd et al. (2002)
	Pioneer Valley, Proserpine	Thorburn et al. (2003)
	Pioneer Valley, Proserpine	McNeil and Raymond (2011) ^{1,2}

¹ Study based on data from the Queensland Government's groundwater database; ²Note, total N (TN) as reported, was based on and equated to, nitrate-N.

In the late 1990s, an extensive survey of groundwater concentrations of nitrate in cane-growing areas included 271 bores in the Mackay–Whitsunday area, 397 bores in the lower Burdekin, and 212 bores in the Wet Tropics (Thorburn et al. 2003). Across all areas, analysis of N isotope ratios ($\delta^{15}\text{N}$) suggested that fertilisers were the likely source of the nitrate in approx. half of the bores in which nitrate concentrations were >4.5 mg nitrate-N/L. Sources of nitrate in the remainder of these bores could not be determined, apart from a small percentage of cases (mostly in the southern GBR region, outside the scope of this review) in which the isotope ratios suggested an organic source (e.g.,

³ Note that unless stated otherwise, nitrate concentrations are reported hereafter on the basis of the N content (not the total mass of nitrate); i.e., as units of mg nitrate-N/L. Nitrite concentrations likewise are reported as mg nitrite-N/L. The conversions are: 1mg nitrate-N/L \equiv 4.43 mg/L of nitrate; and 1mg nitrite-N/L \equiv 3.29 mg/L of nitrite. For example, 10 mg nitrate-N/L multiplied by 4.43 gives 44.3 mg/L of nitrate. Similarly, 11.3 mg nitrate-N/L is equivalent to 50 mg/L of nitrate (which is the Drinking Water Guideline concentration, Table 3.3).

drainage from septic systems or feedlots). Overall, 5% of groundwater samples from both the lower Burdekin and the Pioneer Valley had nitrate concentrations >11.3 mg nitrate-N/L (the Australian Guideline for drinking water quality, ANZECC & ARMCANZ 2000), while a further 15% in the Pioneer Valley and 9% in the lower Burdekin exceeded 4.5 mg nitrate-N/L (Thorburn et al. 2003).

In comparisons across 15 major agricultural areas in Australia between 1993 and 1998, the Pioneer Valley ranked 3rd highest in median groundwater nitrate concentration (around 1 mg nitrate-N/L) and the lower Burdekin 7th highest (approx. 0.5 mg nitrate-N/L), although the numbers of bores monitored and samples taken in each area were not reported (Budd et al. 2002). A median nitrate concentration of 1.1 mg nitrate-N/L was similarly reported for 46 groundwater samples taken in 1997 at different locations across the Pioneer Valley, at depths ranging from 5.5 m to 32 m (Baskaran et al. 2002).

For the lower Burdekin, analysis of groundwater nitrate data from the Queensland Government's GWDB gave an overall mean nitrate concentration (1970–2005, 714 bores) of 1.3 mg nitrate-N/L and a mean since 1990 of 2.0 mg nitrate-N/L. There was a high degree of spatial variability, with high nitrate concentrations clustered in two areas; i) west of the Burdekin River between Clare and Mt Kelly, and ii) near Home Hill (Barnes et al. 2005). Groundwater nitrate concentrations in the lower Burdekin were shown to vary from year to year and with depth: high concentrations (57 bores) were found only within the top 25 m, while concentrations below 30 m were negligible (Thayalakumaran et al. 2008). Based on the mean concentration since 1990, the total aquifer load of nitrate-N was estimated to be 29,355 tonnes (Barnes et al. 2005). Furthermore, nitrate concentrations appear to be increasing with time, at a rate equivalent to 0.06 mg nitrate-N/L/y. Rising trends in nitrate concentrations have also been reported for the Pioneer and the Herbert (McNeil and Raymond 2011).

In a recent initiative in the lower Burdekin, cane-growers participated voluntarily in regular sampling and analysis of nitrate (and salinity) in groundwater from their bores. In total, 962 samples were taken over a twelve-month period, from 409 bores on 313 farms across the lower Burdekin floodplain (BBIFMAC 2012). Overall, around 40% of the samples contained nitrate at concentrations >5 mg nitrate-N/L. Some degree of spatial variation in nitrate concentrations was evident, as was a tendency for concentrations to vary seasonally. In some bores, concentrations fluctuated markedly over a period of weeks (e.g., by around 10–15 mg nitrate-N/L), while concentrations in other bores on the same property remained relatively constant. Of concern was the finding that 22% of samples contained nitrate at >10 mg nitrate-N/L (equivalent to 44 mg/L of nitrate), which is close to the guideline limit for domestic consumption, particularly for infants (Table 3.2). The spatial coverage and frequency of sampling in this study gave valuable insights into nitrate dynamics in the lower Burdekin floodplain, which rarely can be achieved by regular monitoring programs. Continued monitoring would assist considerably in further understanding the interactions between aquifer dynamics, seasonal rainfall patterns, and on-farm N and irrigation management.

A recent geochemical assessment of potential areas of groundwater discharge in the lower Burdekin found nitrate concentrations were low near the coast of Bowling Green Bay (elevation ≤ 3 m, 48 sites), with a median concentration of 0.004 mg nitrate-N/L (Lenahan 2012). This was consistent with results of previous monitoring in the same area, which found nitrate levels to be negligible (Thayalakumaran et al. 2008). Median concentrations were somewhat higher at ten riparian sites (≤ 150 m from a stream channel) and four sites within the floodplain (≤ 3 km from a riparian zone) at 0.09 and 0.57 mg nitrate-N/L, respectively (Lenahan 2012). Under the Reef Protection Program, further monitoring has commenced at these sites to gain more insights into spatial and temporal variability of nitrate; the monitoring also includes measurement of other nutrients, pesticides and geochemical constituents.

Groundwater nitrate concentrations were relatively low in areas of the Wet Tropics with mean annual rainfall ≥ 3500 mm: no samples exceeded 11.3 mg nitrate-N/L and only a small percentage was >4.5 mg nitrate-N/L (Thorburn et al. 2003). This was consistent with results for the lower Johnstone, where the median groundwater concentration was 0.33 mg nitrate-N/L, in 96 bores that were sampled one or more times between 1992 and 1997 (Hunter et al. 2001). However, nitrate concentrations were somewhat higher in areas of the Wet Tropics that receive less rainfall (around 2000 mm/y), with

concentrations in 4% of groundwater samples from both the lower Herbert and the Mulgrave–Russell exceeding 11.3 mg nitrate-N/L; and a further 4% and 31% respectively, exceeding 4.5 mg nitrate-N/L (Thorburn et al. 2003).

In general, median nitrate concentrations in river systems and inshore waters of the Reef lagoon tend to be very much lower than those in corresponding aquifers. For example, median nitrate concentrations in 10 rivers from the Burdekin River north were all <0.15 mg nitrate-N/L (most <0.1 mg nitrate-N/L) (Furnas 2003), while those in inshore waters were lower again by more than an order of magnitude (Furnas and Brodie 1996, Schaffelke et al. 2012). This is reflected in the concentrations (trigger values) recommended by the Australian Water Quality Guidelines for protecting aquatic ecosystems in surface waters of tropical Queensland, that range from 0.002 mg oxidised-N/L (inshore marine waters) to 0.03 mg oxidised-N/L (estuaries) (Table 3.1). Median groundwater nitrate concentrations in the Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas exceed these trigger values to a significant extent, thus highlighting the need for effective attenuation within aquifers or transition zones to minimise loads discharged to receiving surface waters.

*Ammonium*⁴

Concentrations of ammonium have been infrequently monitored in groundwater and typically have been found to be low; e.g., as reported for the lower Johnstone (Hunter et al. 2001), the Don/Bowen area (Baskaran et al. 2001) and the Pioneer (Baskaran et al. 2002). In all three studies, concentrations were generally ≤ 0.01 mg ammonium-N/L, although one or more bores in each area showed concentrations in the range of 1–5 mg ammonium-N/L. In the Don, four bores that consistently had high ammonium levels also had low concentrations of DO (≤ 0.21 mg/L) and negligible levels of nitrate (Baskaran et al. 2001). This coincidence of elevated ammonium (up to 4 mg ammonium-N/L) and low DO and nitrate levels was similarly observed in two studies in the lower Burdekin aquifer (Thayalakumaran et al. 2008, Lenahan 2012) and is discussed further in Section 4.1. The latter study found that median groundwater concentrations of ammonium in the lower Burdekin ranged from below the detection limit (4 floodplain sites) to 0.27 mg ammonium-N/L (48 sites near the coast) (Lenahan et al. 2012).

3.4 Phosphorus

In comparisons across 15 major agricultural areas in Australia (1993–1998), the lower Burdekin was ranked the highest in median groundwater total dissolved P (TDP⁵) concentration, at approx. 0.15 mg P/L (although bore locations and numbers of samples taken were not reported): high concentrations tended to occur in shallow aquifers (Budd et al. 2002). A recent study in the lower Burdekin found that median groundwater concentrations of filterable reactive P (FRP⁵) at ten riparian sites, four floodplain sites, and 48 near-coastal sites, ranged from 0.03 to 0.06 mg P/L (Lenahan 2012). As noted above, further monitoring of groundwater P concentrations is now in progress at these potential areas of groundwater discharge in the lower Burdekin (S. Vardy, pers. comm.).

The Pioneer Valley ranked 4th highest in the above Australia-wide survey, with a median groundwater TDP concentration of approx. 0.08 mg P/L (Budd et al. 2002). A Pioneer Valley survey in 1997 (46 bores) found median groundwater concentrations of TDP and FRP were 0.07 mg P/L and 0.032 mg P/L, respectively, at depths ranging from 5.5 m to 32 m (Baskaran et al. 2002). Median TDP and FRP concentrations for the lower Burdekin and the Pioneer Valley in these studies exceeded by a wide margin, the respective trigger values recommended by the Australian Water Quality Guidelines for the protection of surface water ecosystems in the Queensland tropics (Table 3.1).

⁴ Note that unless stated otherwise, ammonium concentrations are reported hereafter on the basis of the N content (not the total mass of ammonium); i.e., as units of mg ammonium-N/L. The conversion is: 1mg ammonium-N/L is equivalent to 1.3 mg/L of ammonium.

⁵ Total dissolved P (TDP) of a water sample represents all P that passes through a filter of defined pore size (e.g., 0.45 μm); filterable reactive P (FRP) is the component of the TDP that comprises simple inorganic phosphates (see Glossary).

By contrast, groundwater TDP and FRP concentrations in the lower Johnstone were considerably less than in the lower Burdekin and the Pioneer, with respective median concentrations across 96 bores of 0.03 mg P/L and 0.012 mg P/L (sampled 1992–1997) (Hunter et al. 2001). Nevertheless, these median values also exceeded respective guideline trigger values, except possibly those for protecting tropical wetland ecosystems (Table 3.1).

3.5 Herbicides

Residues of the PSII herbicide atrazine and its breakdown product desethyl atrazine (DEA) were the only compounds detected in a survey of 40 bores in the lower Burdekin (1992–1993) in which approx. 80 pesticides were screened (Keating et al. 1996). Although the frequency of positive detections was high in 1992 (76%), atrazine concentrations in both years were generally low, with 50–75% of positive detections <0.1 µg/L, well below the trigger value for protecting 95% of freshwater species in surface waters (Table 3.2). Most samples had a low DEA/atrazine ratio (80% of ratios were <1.0), suggesting rapid leaching of atrazine.

A recent assessment of pesticide residues in groundwater in the lower Burdekin was targeted strategically at locations close to potential riverine and coastal discharge zones (16 and 37 bores, respectively) (Shaw et al. 2012). Overall, 38% of samples showed positive detections of one or more pesticides, including residues of the PSII herbicides diuron, hexazinone, atrazine and two breakdown products of atrazine, DEA and desisopropyl atrazine. Mean concentrations of diuron and DEA were 0.07 µg/L, while mean concentrations of the other three residues were around 0.02 µg/L. In all cases, the maximum detected concentrations of PSII herbicides were considerably less than respective trigger values for ecosystem protection (Table 3.2) and did not exceed drinking water guidelines (Table 3.3). The herbicide metolachlor was also detected at low concentration (0.009 µg/L) in one sample. It is worth noting that improvements to water analysis techniques over the past decades have progressively lowered pesticide detection limits, and this should be taken into account when comparing contemporary rates of detection with those from previous studies. Further monitoring to better understand spatial and seasonal patterns of herbicide residue concentrations in groundwater was recommended at these locations, particularly given the use of groundwater for domestic consumption in this area and its proximity to the Reef lagoon (Shaw et al. 2012). As noted above, further monitoring initiated in these areas under the Reef Protection Program will provide more insights into the dynamics of herbicides in groundwater in areas of potential discharge.

Thirty per cent of the 46 bores sampled in 1997 in the lower Pioneer Valley showed positive detections of one or more of the 154 pesticides and related compounds screened (Baskaran et al. 2002). The herbicide diuron was most commonly detected (20% of samples), followed by atrazine and its breakdown product, DEA. Bromacil, ametryn and hexazinone were also detected but in <10% of samples. Concentrations were generally low: except for one incidence of 5.2 µg/L of bromacil, all residues were detected at concentrations ≤1.8 µg/L, with most <0.1 µg/L. Concentrations of diuron at four sites exceeded the indicative interim water quality guideline for protecting freshwater species, but no sites exceeded the diuron guideline for protecting marine species (Table 3.2).

Atrazine was detected in three of sixteen bores surveyed in the Johnstone Basin in the Wet Tropics in 1995 (at concentrations of 0.4–0.7 µg/L), with no residues of other PSII herbicides detected. Similarly in 1996, atrazine was the only residue detected (one bore), at 0.3 µg/L (Hunter et al. 2001).

3.6 Organic carbon

Dissolved organic carbon is critical to microbial processes in subsurface environments (e.g., nutrient cycling and attenuation, and herbicide decomposition) but it is not commonly measured in groundwater water quality monitoring programs. It occurs naturally in groundwater at low concentrations (typically <5 mg C/L) although concentrations in contaminated aquifers may be much higher; e.g., associated with leachate from landfill (Rivett et al. 2008). The review found four reports of DOC concentrations in groundwater within the study areas. In two of these studies, DOC

concentrations were generally low, with a median of <0.5 mg C/L in the Pioneer (Baskaran et al. 2002) and 1.1 mg C/L in the Don (Baskaran et al. 2001), although there were occasional exceptions. The highest DOC concentration reported for the Pioneer was 23 mg C/L and for the Don, 11 mg C/L.

By comparison, levels of DOC were very much higher in the lower Burdekin in 2003–2004 (Thayalakumaran et al. 2008). Most of the approx. 30 bores monitored were in cane-growing areas relatively close to the coast. Concentrations of DOC in groundwater ranged from 4 to 82 mg C/L, with a high proportion >20 mg C/L. Thayalakumaran et al. (2008) considered the high DOC levels in the lower Burdekin may have been associated with the leaching of sugarcane juices lost at harvest, when DOC concentrations up to 300 mg C/L have been reported in post-harvest runoff water (Bohl et al. 2002). However, 48 groundwater samples taken more recently (2011) in the same area of the lower Burdekin had very much lower DOC concentrations, with a median value below the limit of detection and a maximum of 4 mg C/L (Lenahan 2012). The contrast between these two sets of results is surprising and suggests that geochemical processes are dynamic in this part of the lower Burdekin aquifer. It also highlights the need for further investigation to better understand temporal and spatial variations in DOC concentrations and the inter-relationships between nitrate, DOC and other electron donors (reduced iron, manganese and sulfur) that can facilitate nitrate attenuation (discussed in Section 4.1).

3.7 Summary of key points

- Except for nitrate, there have been few studies of N, P and herbicides in groundwater across the Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas, particularly over the last ten years
- Ten studies reported on groundwater concentrations of nitrate, the most extensive of which (in the late 1990s) covered all three study areas and found that overall, nitrate from approx. half of the bores with elevated nitrate levels (>4.5 mg nitrate-N/L) was likely to have been derived from fertilisers
- Analysis of long-term nitrate records for the lower Burdekin suggest concentrations appear to be increasing with time, with similar trends also reported for groundwater in the Pioneer Valley and the Herbert (in the Wet Tropics)
- In the lower Burdekin, a recent assessment found low concentrations of nitrate in groundwater in potential discharge areas near the coast of Bowling Green Bay; which was consistent with results of previous monitoring in the same area
- Groundwater nitrate concentrations in the lower Burdekin were shown to vary from year to year and with depth, with high concentrations found only within the top 25 m; a survey by growers found concentrations in some bores fluctuated markedly over a period of weeks
- Groundwater nitrate concentrations were relatively low in high rainfall parts of the Wet Tropics
- An Australia-wide survey of major agricultural areas in the mid-1990s found elevated P levels in groundwater in the lower Burdekin and the Pioneer Valley, with the Burdekin ranked highest and the Pioneer 4th highest, of the fifteen areas surveyed
- Recent monitoring of groundwater in areas of potential discharge in the lower Burdekin found residues of several herbicides, but only at low concentrations

4. Nutrient and Herbicide Processes and Links to On-farm Management

Many factors influence the fate of N, P and PSII herbicides in soils and deeper subsurface environments, including natural processes (e.g., seasonal fluctuations in rainfall and drainage) and anthropogenic activities (e.g., fertiliser, herbicide and irrigation management). They are subjected to a variety of transformation and degradation processes, some of which may temporarily or permanently reduce their concentrations in groundwater, thereby attenuating loads transported to receiving environments such as the Reef lagoon. The following discussion gives an overview of key pathways and processes that affect the transport, transformation and degradation of N, P and PSII herbicides in the root zone and in deeper subsurface environments, together with the links to on-farm management practices. Where possible, emphasis is placed on reviewing relevant research conducted in the study areas.

4.1 Nitrogen

Nitrogen is a natural constituent of soils, with most N being present in surface layers as organic N (Ladd and Russell 1983). The microbial processes of decomposition and mineralisation release ammonium and nitrate from the soil organic N pool, with these mineral N forms being available for uptake by crops and other organisms (Fig. 4.1). Microbial uptake cycles mineral N back into the organic N pool. Nitrogen is commonly applied to sugarcane crops to supplement the soil's natural N reserves and optimise yields, with the additional N being derived from a variety of sources including legume crop residues, organic amendments (e.g., mill mud and dunder) and manufactured fertilisers such as urea. In saturated or near-saturated soils, bioavailable organic C can provide a source of electrons to support the microbial process of denitrification, which converts nitrate to dinitrogen (N_2) and nitrous oxide (N_2O) gases (Ladd and Russell 1983). Associative N fixation (bacterial conversion of N_2 to ammonium) is not currently considered a significant source of N in cane (Thorburn 2004).

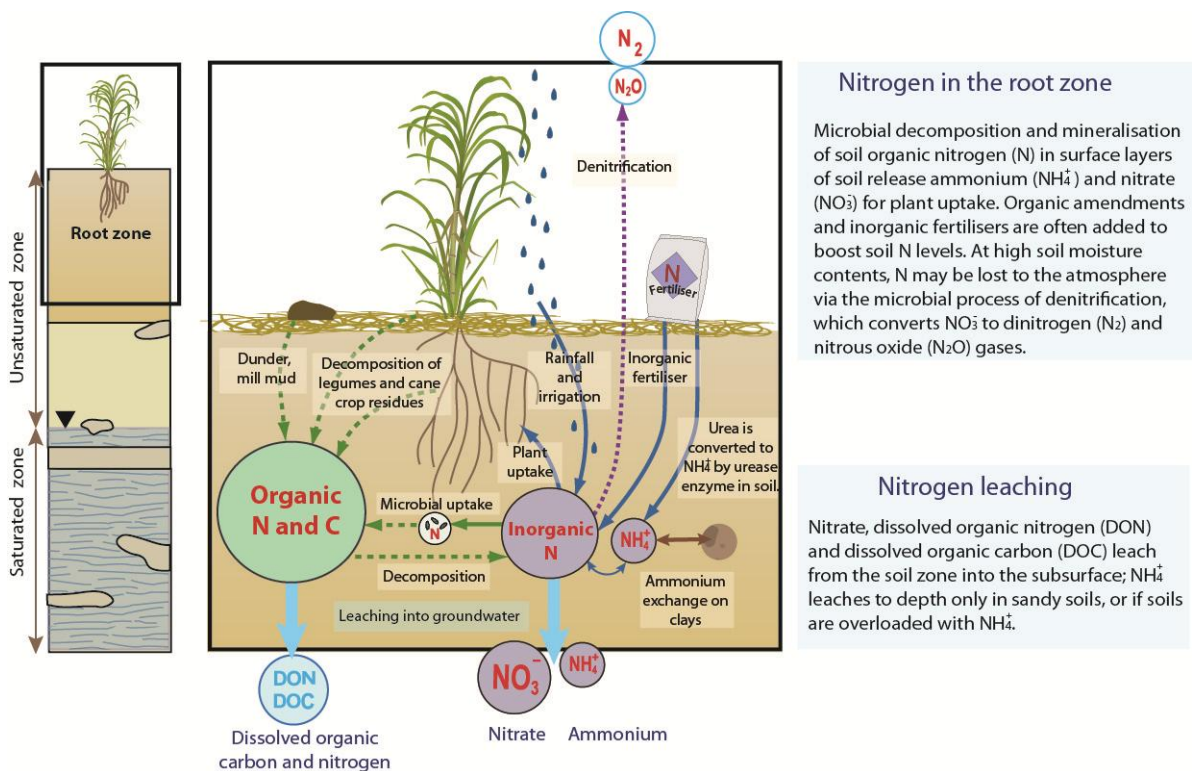


Figure 4.1. Conceptualisation of nitrogen dynamics in the root zone under cane. Adapted from Thorburn et al. (2005).

Nitrate is a highly mobile form of N and is the predominant form likely to be leached below the root zone (Ladd and Russell 1983). Ammonium is generally much less mobile as it is held by cation exchange sites on clay particles and/or organic matter that are present in most soils. However, ammonium leaching may occur in sandy soils, or less commonly, in non-sandy soils if all exchange sites are saturated. Dissolved organic N (DON) may also leach although the amount leached below the root zone under natural conditions is likely to be small. More DON may be leached following applications of organic by-products like mill mud and dunder, although field studies are needed to confirm this. Similarly, amounts of DOC leached below the root zone are generally quite small under natural conditions but as noted previously, leaching of DOC potentially may increase following mill mud or dunder applications, or from cane juices lost at harvest (although further research is needed to quantify this). Key processes and pathways that influence the fate of N in subsurface environments below the root zone are summarised in Table 4.1 and Fig. 4.2.

Table 4.1. Summary of key reaction pathways involved in nitrogen transformations

Process	Pathway	Conditions
Denitrification <i>Overall chemical equation</i> ¹	Nitrate → Nitrite → Nitrous oxide → Dinitrogen $5\text{CH}_2\text{O} + 4\text{NO}_3^- + 4\text{H}^+ \rightarrow 2\text{N}_2 + 5\text{CO}_2 + 7\text{H}_2\text{O}$	Anaerobic
DNRA ²	Nitrate → Nitrite → Ammonium	Anaerobic
Anammox	Nitrite + Ammonium → Dinitrogen	Anaerobic
Organic matter decomposition (mineralisation)	Organic N → Ammonium	Anaerobic & aerobic
Microbial uptake (immobilisation)	Ammonium → Organic N Nitrate → Organic N	Anaerobic & aerobic
Nitrification	Ammonium → Nitrite → Nitrate	Aerobic

¹ Commonly cited equation for denitrification using glucose as substrate (Beauchamp et al. 1989); ² Dissimilatory nitrate reduction to ammonium

Nitrate transformation and attenuation

Denitrification is the dominant mechanism for removing nitrate from subsurface environments below the root zone. It is a respiratory process carried out by micro-organisms that require anaerobic conditions and the presence of bioavailable organic carbon (Knowles 1982, Robertson and Groffman 2007). Dissolved oxygen concentrations of <1–2 mg/L are required for denitrification to proceed, associated with a redox potential (Eh) of around +230 mV or lower (Rivett et al. 2008). These conditions are most likely to occur in the saturated zone but may also occur at microsites within less permeable areas of the unsaturated zone where DO concentrations are low, e.g., due to high levels of microbial activity (Knowles 1982).

Some denitrifiers can use reduced forms of manganese (Mn^{2+}), iron (Fe^{2+}) and sulfur (S^{2-}) instead of organic carbon (Korom 1992) but most use organic carbon if available, both for energy (via denitrification) and for cellular growth. Denitrifying bacteria are ubiquitous in soils and sediments and have been found in aquifers at depths up to 450 m (Rivett et al. 2008). Dinitrogen (N_2) gas is the ultimate end product of denitrification (Table 4.1, Fig. 4.2) but significant amounts of the ‘greenhouse’ gas nitrous oxide (N_2O , the penultimate end product) can also be released under certain conditions (e.g., low pH, high nitrate, relatively high oxygen levels) (Groffman et al. 2000).

From the chemical equation for denitrification (Table 4.1) it can be calculated that theoretically, 1 mg C/L of DOC (as glucose) is sufficient for complete denitrification of 0.93 mg nitrate-N/L (Rivett et al. 2008), although note that the DOC/nitrate-N ratio required varies depending on the DOC substrate (Beauchamp et al. 1989). This theoretical estimate does not allow for competing microbial demands for DOC (e.g., for growth) so in practice, a higher DOC/nitrate-N ratio would be required for complete denitrification (Beauchamp et al. 1989). Moreover, DOC naturally present in soils and sediments occurs in a variety of forms of differing bioavailability and suitability as a substrate for denitrification, with many forms being less bioavailable than glucose. For these substrates, an even higher DOC/nitrate-N ratio would be needed for complete denitrification (Beauchamp et al. 1989).

Pesticides encompass a broad suite of different organic compounds, which is reflected in the range of their reported effects on denitrification, from stimulatory to inhibitory, to no effect at all (reviewed by Rivett et al. 2008). Elevated DOC levels (e.g., following application of organic amendments) would likely enhance denitrification rates, but at very high levels they may tend to favour the process of DNRA instead (Table 4.1 and Fig. 4.2, also see below) (Rivett et al. 2008).

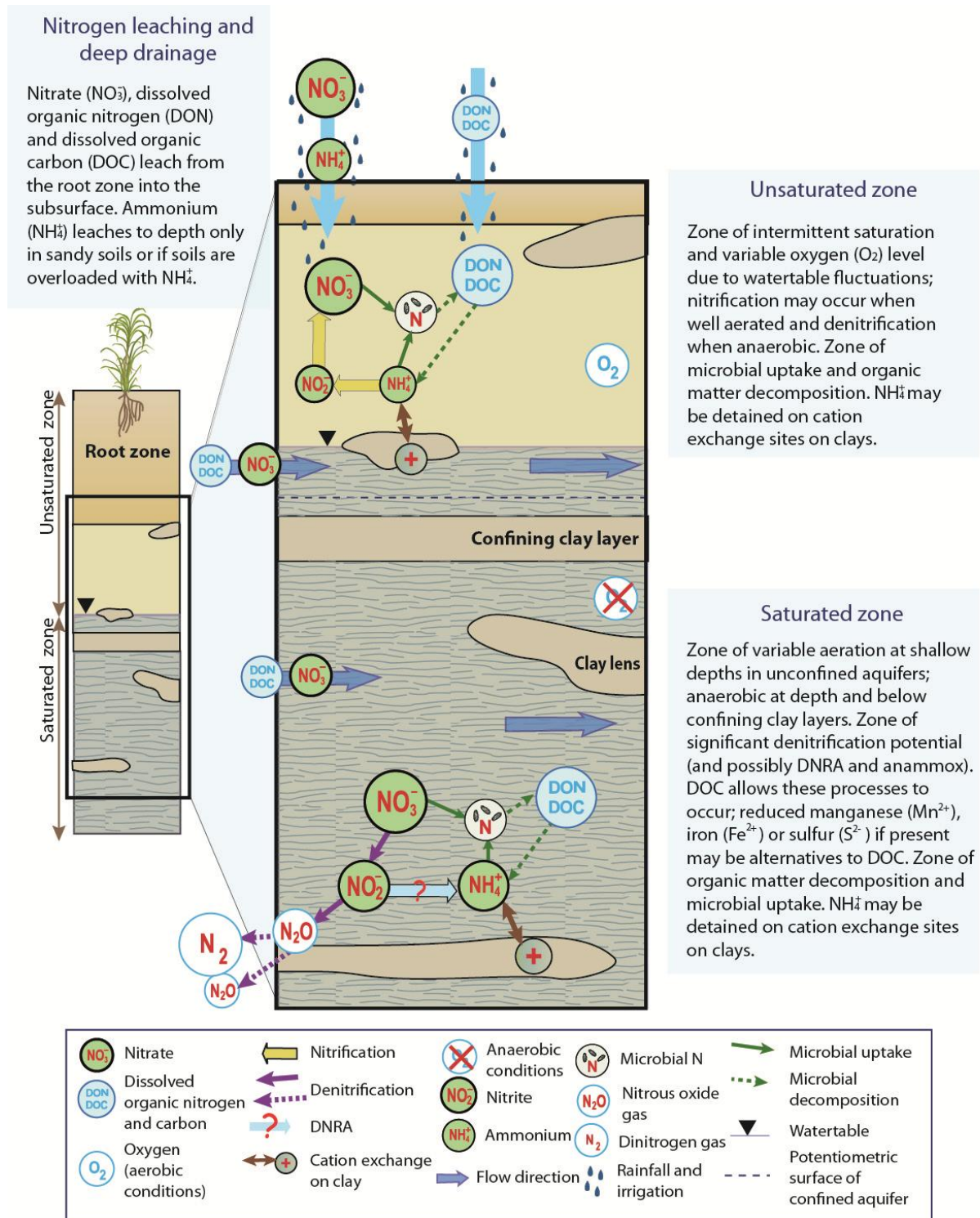


Figure 4.2. Conceptualisation of processes involved in the subsurface transport, transformation and attenuation of nitrogen in the unsaturated and saturated zones. (Refer also to Table 4.1).

Denitrification is spatially heterogeneous in aquifers with rates dependent on factors such as aquifer mineralogy and hydrogeology, temperature and the amount of nitrate available. It is difficult to measure actual denitrification rates in the field, although *in situ* rates have been reported from a number of studies (mainly in cool temperate regions) and were reviewed by Korom (1992).

Dissimilatory nitrate reduction to ammonium (DNRA) is another potential mechanism for nitrate attenuation, in which ammonium is the end product (Table 4.1, Fig. 4.2). The DNRA mechanism has been known for at least 30 years (Tiedje et al. 1982) but its occurrence has not been widely reported and it is considered rarely to be the dominant mechanism of nitrate attenuation in aquifers, except perhaps in environments highly enriched with DOC (Beauchamp et al. 1989, Rivett et al. 2008). It occurs under similar conditions to denitrification but unlike denitrifiers, the bacteria that carry out DNRA require strictly anaerobic conditions (Burgin and Hamilton 2007). Another difference is that, in contrast to denitrification, the end product of DNRA (ammonium) is retained within the aquifer, where under oxidising conditions it may subsequently be converted back to nitrate (Korom 1992).

There is considerable interest in the potential of riparian and wetland buffers to mitigate groundwater fluxes of nitrate entering surface waters (e.g., reviews of Hill 1996, Mayer et al. 2007). The greatest potential for nitrate attenuation tends to occur in relatively low lying and low-gradient landscape settings where shallow groundwater passes through riparian or wetland soils of moderate hydraulic conductivity (Hunter et al. 2006, Rassam et al. 2008, Rassam and Pagendam 2009). These conditions provide sufficient residence time in the DOC-enriched root zone of riparian and wetland soils for denitrification to be effective (Fig. 4.3). Residence times are likely to be too short in highly conductive soils, while low conductivity soils allow for only a small groundwater flux. Stream-bed sediments in the benthic and hyporheic zones may provide further opportunities for denitrification, not only for in-stream attenuation but also for groundwater that by-passes the riparian zone and enters the stream through these zones (Fig. 4.3). The denitrification potentials of sixteen contrasting riparian sites in south-east Queensland, Victoria and Western Australia were around 2 mg N/kg dry soil/day (average of all sites) in benthic and hyporheic sediments; while rates in riparian soils were around 6 mg N/kg dry soil/day near the surface, and ≤ 1 mg N/kg dry soil/day at depth (Fellows et al. 2007).

An underlying premise of conceptual models of riparian zones as hotspots for denitrification (as shown in Fig. 4.3) is that organic carbon concentrations are much higher and extend deeper in riparian zones that have dense stands of permanent, deep-rooted vegetation, than under short-lived vegetation in cultivated fields. This has been shown to be the case elsewhere (e.g., on a pineapple farm in south-east Queensland; H. Hunter, unpublished). However, it is interesting to speculate whether organic carbon levels beneath sugarcane would necessarily differ so markedly from those under permanent vegetation, given the amounts of sugars reportedly lost at harvest (Bohl et al. 2002) and the amounts of organic-rich amendments (e.g., mill mud) applied in some areas (Section 4.4).

In unconfined alluvial aquifers, seasonal fluctuations in watertable levels can affect not only recharge–discharge dynamics between aquifers and streams, but also redox conditions and geochemical reactions in the zone of intermittent saturation. Surface water recharge of an alluvial aquifer is typically followed by a sequence of microbial reactions that accompany the oxidation of organic C to inorganic C, together with a decline in redox potential. Reactions include: aerobic respiration, denitrification, Mn^{4+} reduction, Fe^{3+} reduction, SO_4^{2-} reduction, and sometimes, methane production (Vinson et al. 2007). Hence, in addition to its role as a substrate for denitrification, DOC may further enhance the denitrification potential of subsurface zones, by increasing levels of other potential electron donors (i.e., Mn^{2+} , Fe^{2+} , S^{2-}) as redox potentials decline. Redox gradients in zones of intermittent saturation thus may be transient and may fluctuate to reflect trends in seasonal stream–aquifer interactions. For example, during spring, infiltration of oxygenated water from a headwater stream in New Mexico increased the redox potential in a shallow alluvial aquifer and resulted in oxidation of Mn^{2+} , Fe^{2+} and S^{2-} (Groffman and Crossey 1999). However, redox conditions were moderately reducing by autumn and supported microbial reduction of these ions back to their reduced states (Groffman and Crossey 1999). Inputs to this system of bioavailable DOC (e.g., low molecular weight organic acids) from organic-rich surface layers were critical, providing both a substrate for microbial metabolism and a source of electrons for reduction reactions (Groffman and Crossey 1999).

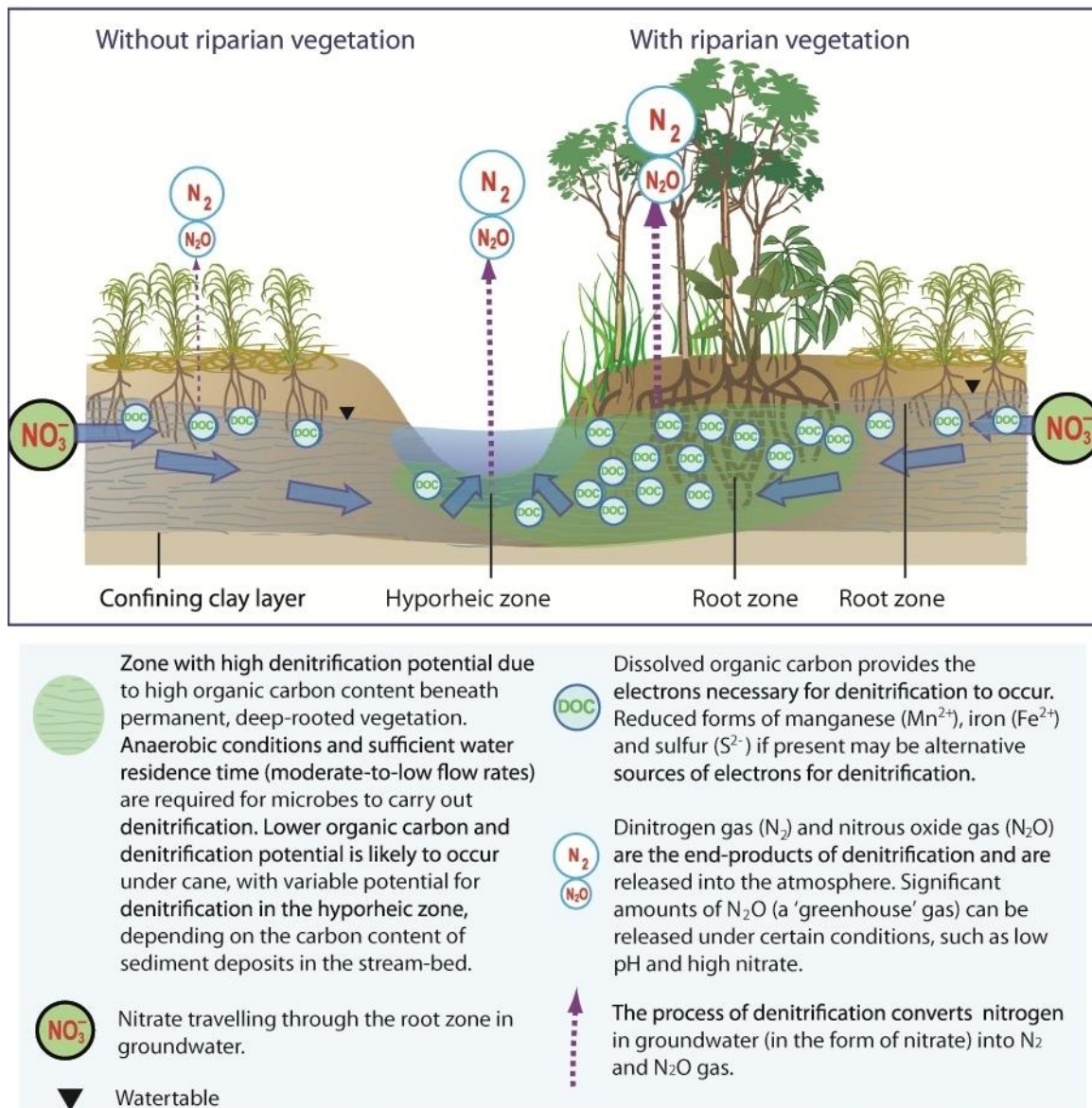


Figure 4.3. Conceptualisation of denitrification in riparian and hyporheic transition zones, where groundwater and stream waters interact. Denitrification can occur similarly in wetland settings.

The groundwater–seawater interface in some situations may present a setting for denitrification similar to riparian areas and wetlands (e.g., where shallow groundwater seeps through silt and clay deposits beneath mangrove forests) while in other cases groundwater may be discharged more rapidly through sandy sediments where there may be much less potential for denitrification. Fluxes of N via SGD can sometimes be comparable to (or greater than) those from rivers, with water residence times and redox conditions in coastal aquifers and sediments identified as key factors that influence the SGD flux of N (Slomp and Van Cappellen 2004). Other factors include the presence of bioavailable DOC (or other electron donors for denitrification) and the redox dynamics of the mixing zone where aerobic or anaerobic groundwater meets aerobic or anaerobic intruded seawater (e.g., as illustrated in Fig. 4.4). Reported daily flux rates of N via SGD vary widely; e.g., from 2.2 mg N/m²/d from an uncontaminated alluvial aquifer in Hawaii, to 742 mg N/m²/d from the alluvium of southern Chesapeake Bay, where the N was derived from fertilisers (reviewed by Slomp and Van Cappellen 2004). In some settings, recirculated seawater rather than fresh groundwater discharge may be the dominant source of the SGD flux, as shown for the nitrate flux from a subterranean estuary in the Gulf of Mexico (Santos et al. 2008).

Depending on prevailing conditions in the aerobic or anaerobic transition zone between groundwater and intruded seawater, the potential transformations of N that may occur encompass the suite of reaction pathways shown in Fig. 4.2 and Table 4.1. These include the coupling of nitrification and denitrification, DNRA, anammox (see below), microbial uptake and organic matter decomposition (Santoro 2010). The extent to which each of these processes occurs in this zone may alter as fresh groundwater mixes with intruded seawater and becomes more saline (Santoro 2010). Conditions in the transition zone may not always be suitable for nitrate attenuation to occur and the SGD flux of N may be high. For example, nitrate concentrations in SGD from an unconfined aquifer in Western Australia were two orders of magnitude higher than those in receiving waters of a small coastal lagoon, with the SGD nitrate flux estimated to be sufficient to replace the total nitrate load in the lagoon about every eight days (Johannes and Hearn 1985).

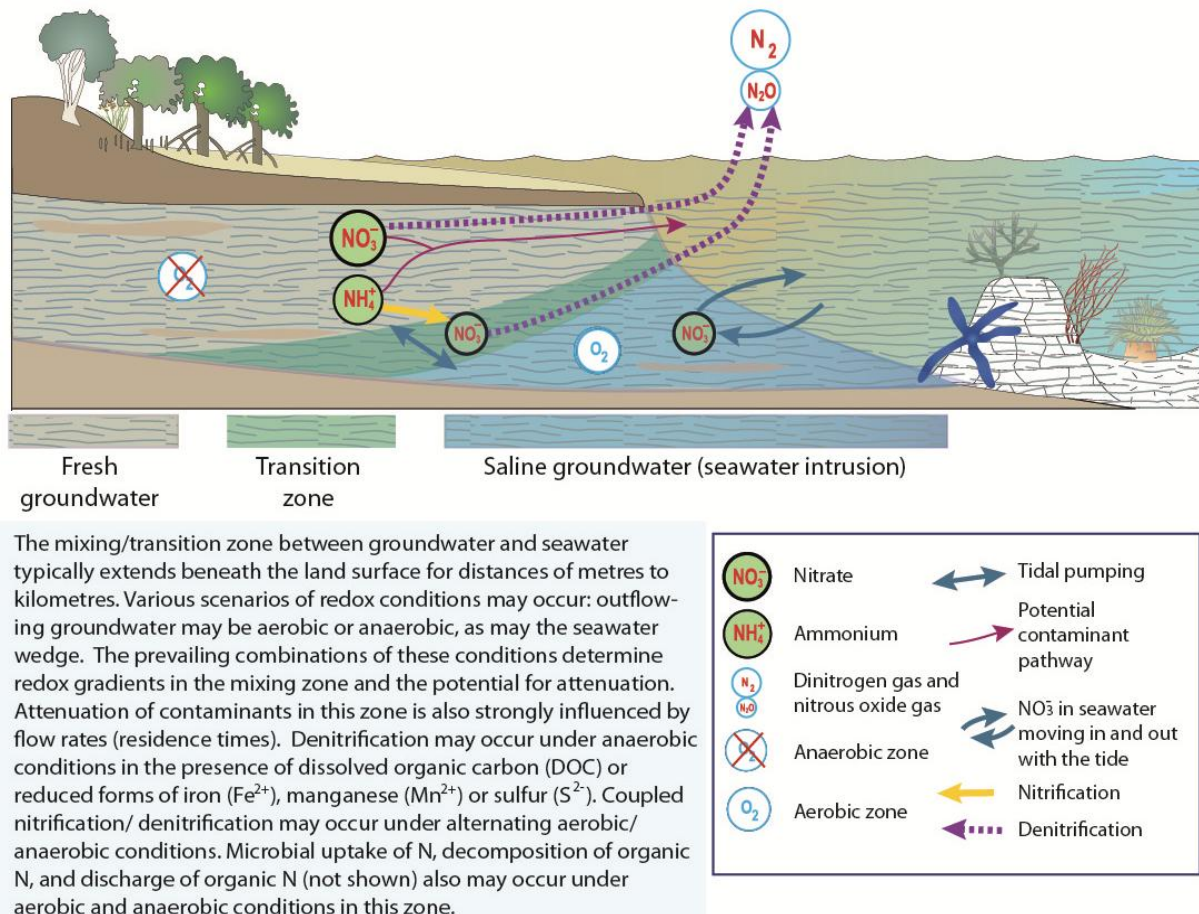


Figure 4.4. Conceptualisation of one scenario of potential nitrogen attenuation processes in the transition zone, in which anaerobic fresh groundwater mixes with intruding aerobic seawater. Nitrogen attenuation may possibly also occur in anaerobic waters in this zone via DNRA and anammox (not shown). Adapted from Slomp and Van Capellen (2004).

Fate of ammonium

Ammonium in the saturated zone (whether produced by DNRA, or by organic matter decomposition, or leached from the surface in sandy soils) would be available for microbial uptake or sorption onto clay minerals. A further potential fate of the ammonium (not shown in Fig. 4.2) is its reaction with nitrite (an intermediate product of denitrification) and conversion to dinitrogen gas by the process known as anaerobic oxidation of ammonium (anammox) (Table 4.1). Identified quite recently, the anammox process has now been demonstrated quite widely in marine sediments (Jetten et al. 2009). Its broader occurrence is still uncertain, although anammox bacteria have recently been reported to be present in abundance at three groundwater sites in Canada (Moore et al. 2011). Ammonium may also be converted to nitrate if conditions are sufficiently aerobic (Fig. 4.2, Table 4.1).

The movement of ammonium through aquifers is not well understood, although detailed isotopic studies in north-eastern USA showed the bulk of the ammonium present in a contaminated groundwater moved down-gradient at a rate one-quarter that of the groundwater velocity (Böhlke et al. 2006). Zones where nitrification and sorption occurred were identified using $\delta^{15}\text{N}$, but no evidence of anammox was found.

Studies in Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas

Nitrate attenuation in the lower Burdekin aquifer

A geochemical assessment of the potential for nitrate attenuation in the lower Burdekin floodplain (57 bores) found groundwater in 55% of the bores had redox conditions suitable for denitrification and/or DNRA (Thayalakumaran et al. 2008). Nitrate concentrations ranged from 0.1 to 14.4 mg nitrate-N/L, with low concentrations found in conjunction with high levels of reduced iron (Fe^{2+}). Negligible levels of nitrate were found in groundwater close to the coast. Maps of areas showing high denitrification potential (i.e., where $\text{DO} < 1 \text{ mg/L}$, $\text{Fe}^{2+} > 1 \text{ mg/L}$ and $\text{Eh} < 225 \text{ mV}$) in both shallow (<15 m) and deep groundwater (>15 m) indicated there was considerable potential for nitrate attenuation, particularly in shallow groundwater in areas along the coastal margin north of the Burdekin River (Thayalakumaran et al. 2008).

A recent study similarly found a high denitrification potential in a large low-redox zone within the lower Burdekin aquifer, extending up to 15 km inland from the coast. Groundwater was characterised by negligible levels of nitrate, low DO (<0.5 mg/L), and elevated concentrations of Fe^{2+} and reduced manganese (Mn^{2+}): Fe^{2+} was present in shallow, low salinity groundwater and Mn^{2+} in deeper, more saline parts of the aquifer (Lenahan 2012).

Both of the above studies reported elevated ammonium concentrations in groundwater at some locations. Nitrate concentrations were low where ammonium concentrations were high (up to 8 mg ammonium-N/L), suggesting the possible occurrence of DNRA, particularly given the occurrence of high DOC levels (up to 82 mg C/L) and low redox potential in these areas (Thayalakumaran et al. 2008). However, decomposition of organic-rich marine deposits may be an alternative explanation of the elevated ammonium concentrations, which were found in deep, saline waters more than 1,000 years old (Lenahan 2012). As noted in Section 3.6, groundwater DOC concentrations appear to be highly variable in the lower Burdekin aquifer, with markedly higher concentrations found in 2003 and 2004 (Thayalakumaran et al. 2008) than in 2011 (Lenahan 2012).

A high potential for nitrate attenuation was also found at riparian sites in the lower Burdekin floodplain, near areas of groundwater discharge to the Burdekin River and Barratta Creek (Lenahan 2012). At both locations, concentrations of DO decreased towards the stream, while levels of Fe^{2+} , Mn^{2+} and DOC increased, resulting in a low-redox zone with high denitrification potential, immediately adjacent to the stream. Fe^{2+} and Mn^{2+} were considered likely to be the principal electron donors for denitrification, since concentrations of DOC in groundwater were relatively low, even close to the streams (Lenahan 2012). Modelling of processes in the 25 m of riparian zone adjacent to Barratta Creek suggested a groundwater residence time of around 260 days, based on conditions in August 2011. This was sufficient for complete denitrification of 2.3 mg nitrate-N/L when added in a scenario of a single input of nitrate (i.e., not a continuous loading) (Lenahan 2012).

Important insights into geochemical processes in the lower Burdekin aquifer have been gained from these studies, which are the first such investigations to be conducted in aquifers of the GBR region. Geochemical conditions in groundwater discharge areas suggest a high potential for nitrate attenuation and the possibility that fluxes of nitrate discharged from these areas may be negligible. However, much further investigation is required to reduce current uncertainties before such broad conclusions can be drawn. Key issues to be resolved include the need to better define; i) groundwater flow paths to the marine environment and the possible role of preferential flow paths; and ii) spatial and temporal variations in redox conditions in these environments and the processes that underlie them (Lenahan 2012).

Nitrate attenuation potential in riparian zones and wetlands of the Wet Tropics

Groundwater–surface water relationships under different seasonal conditions were examined in a riparian buffer beside Behana Creek in the Mulgrave River catchment (Connor et al. 2012). It was concluded that the site was unlikely to be effective in nitrate attenuation: the hydrology was complex and dynamic during the wet season, with groundwater discharged rapidly to the stream; while the watertable was several metres deep during the dry season and discharge to the creek was negligible.

A three-year study of a riverine wetland in the lower Tully–Murray catchment similarly concluded that the hydrological conditions at the site were not well suited to nitrate attenuation (McJannet et al. 2012). The wetland was mainly fed by surface water inflows but was groundwater dominated for around two months of the dry season when inflows and outflows were low. While some nitrate attenuation occurred both in the water column and (particularly) in wetland soil during these low flow periods, the losses amounted to <3% of the annual input of N (McJannet et al. 2012). Overall, residence times were thus considered too short for nitrate attenuation to be effective at this site.

Application of a riparian mapping tool in the Tully–Murray catchment found that riparian buffers in mid-sections of the catchment were likely to have the most potential for N loss via denitrification, compared with buffers elsewhere in the river network. This was largely due to the agricultural land use in this area (providing a source of nitrate) and the flat topography (Rassam and Pagendam 2009).

Results of these studies emphasise the importance of the hydrologic setting in determining the denitrification potential of a site. Care should be taken therefore, to understand the hydrology of other riparian and wetland areas in the Wet Tropics (or elsewhere) on a case-by-case basis, when assessing their denitrification potential.

Nitrate losses via leaching, deep drainage and discharge to drains

Nitrogen levels were monitored in soil drainage water at 0.9 m depth under cane for about six months following fertiliser application to a deep, self-mulching medium clay soil in the Sandy Creek catchment of the Mackay–Whitsunday area (Rohde et al. 2011). Concentrations of nitrate, ammonium and urea were not remarkably high from a soil solution perspective (e.g., the highest was 1.8 mg nitrate-N/L, 6 days after application) and it is likely more N may have been accessed by plant roots deeper in the profile. Nevertheless, above-average rainfall resulted in the formation of a shallow perched watertable (<1 m below the soil surface) for six months of the year (Rohde et al. 2011), highlighting the need to minimise N levels in drainage water to protect groundwater quality.

Nitrate losses via subsurface flow were measured over two relatively wet years on a range of soil types in the Ripple Creek area of the lower Herbert catchment in the Wet Tropics, including losses to groundwater (vertical deep drainage) and via lateral flows from shallow perched watertables (0–1 m depth) (Bohl et al. 2000). From an agronomic perspective, N losses to groundwater (17 kg/ha/y) and drains (8 kg/ha/y) were relatively small. However, there was considerable variation between sites and years; e.g., sandy soils on the riverbank showed losses to groundwater of around 70 kg N/ha/y. Further, as noted by the authors, the timing of fertiliser application relative to rainfall may have been an important factor in the results (as may the timing of the monthly to bi-monthly sampling).

Nitrate losses in leachate under commercially-grown sugarcane crops in the Wet Tropics (Mulgrave–Russell catchment) were small, with losses at 1 m depth over three years of ≤ 9.2 kg N/ha over each of three wet seasons (Armour et al. 2012). Less nitrate was leached in the two ratoon crops than in the plant crop, and losses were least when the period between the (once-yearly) fertiliser application and the next deep drainage event was longest. A previous study in the Johnstone catchment (Reghenzani et al. 1996) used somewhat higher N application rates than the above study (viz., 160–170 kg N/ha/y) and estimated leaching losses (>0.6 m depth) of 30 kg N/ha/y, averaged over a plant crop and four ratoons in a trash-retention system: however, the N mass balance suggested that the crops in this study may have later accessed some of this leached N from deeper in the soil profile, thus reducing the overall leaching losses to groundwater. This second study also found that in first ratoon crops, considerably more N leached beneath a mounded-profile row with sub-surface applied urea fertiliser, than beneath a flat-profile row with surface applied urea (Reghenzani et al. 1996).

By contrast with cane, leaching losses of 246 and 641 kg nitrate-N/ha were measured at 1 m depth under bananas, over two crop cycles in the Johnstone catchment. These losses represented 37% and 63% respectively, of fertiliser N applications (710 and 1065 kg N/ha) over the 18-month period (Armour et al. 2012). However, it should be noted that these measurements were made in 1995–1997 and since then the banana industry has achieved up to 40% reductions in N fertiliser application rates (to 310 kg N/ha/y) without apparent loss in yield (Armour et al. 2012).

Monitoring of subsurface drainage of nitrate under bananas in the Tully catchment was conducted over the 6-month wet season (December–May) in each of three years, 2004–2006 (Rasiah et al. 2010). Mean nitrate concentrations across the three seasons were 5.3 mg nitrate-N/L in leachate at approx. 1 m depth in the soil profile; 2.0 mg nitrate-N/L in an adjacent drain at approx. 3 m depth; and 4.1 mg nitrate-N/L in groundwater. Wet-season nitrate concentrations at 1 m depth in this study were very much lower than those reported under fertilised bananas in the above study of Armour et al. (2012), possibly due to the much lower rates of fertiliser application used in the more recent Tully study (300–450 kg N/ha/y).

Nitrate on anion exchange sites in Wet Tropics soils

Red Ferrosol soils are quite widely distributed in the Johnstone catchment, with some shown to have an anion exchange capacity at depth that allows them to accumulate considerable amounts of nitrate. Across 19 such soils under sugarcane in the Johnstone Basin, an average of 1,550 kg nitrate-N/ha was held in the profile at depths from 1–12 m, with the bulk of the nitrate held at depths of 4–10 m, well below the root zone (Rasiah et al. 2003a). By contrast, negligible amounts of nitrate were held by the same soil type under rainforest. These soils were estimated to have the capacity to hold up to a further 10,800 kg nitrate-N/ha in the profile.

Laboratory leaching experiments on such a Ferrosol soil from the Johnstone catchment indicated that nitrate was slowly released from anion exchange sites as rainwater passed through, with tens of years estimated as the likely time required for the nitrate reserves to be depleted from these soils *in situ* (Donn and Menzies 2005). The exchange capacity was insufficient to retain all nitrate passing through the soil. Thus, while groundwater nitrate concentrations are buffered to some extent by the anion exchange capacity of these soils, the attenuation is only temporary. From a water quality management perspective, considerable lag times may therefore be expected before improved N management by cane and banana growers would be reflected in significant reductions to groundwater and stream nitrate loadings.

Modelling analysis showed nitrate delivery to the Johnstone River system to be dominated by baseflow (groundwater) processes: during drier months nitrate is supplied from deeper aquifers of relatively low nitrate concentration, but when groundwater levels rise rapidly following major rainfall events, nitrate is supplied from all aquifers, including the Ferrosols at 2–12 m depth that are enriched with nitrate under cane (Walton and Hunter 2009). It was estimated from 21 to 81 kg nitrate-N/ha was discharged from these soils to streams over 10–21 day periods as groundwater levels receded following such events (Rasiah et al. 2003b). These processes contribute to the elevated stream nitrate levels that are found in cane-growing areas of the Johnstone catchment (Hunter and Walton 2008).

Currently it is not known whether other agricultural soils in the Wet Tropics may similarly hold large reserves of nitrate deep in the profile. A recent estimate indicates that around 10% of cane grown in areas from the Herbert north is on Ferrosols, most with the potential for anion exchange at depth. They occur mainly in the Tully and Johnstone areas and to a lesser extent the Mulgrave–Russell. It is likely that a proportion of other cane-growing soils in the Wet Tropics (e.g., some Dermosols and Kurosols) also may have anion exchange properties at depth (B. Harms, pers. comm.). This issue warrants investigation to determine the extent of nitrate accumulation at depth in these soils so that the implications for reducing stream nitrate loads in affected areas can be assessed.

4.2 Phosphorus

Organic P reserves naturally present in soils are derived from decomposition of residues of plants, animals and soil biota and are recycled through the soil microbial biomass (Fig. 4.5). Typically, most P is present in the surface layers of soil as organic P (Probert et al. 1983), with the microbial processes of decomposition and mineralisation releasing inorganic P that can be taken up by plants and other organisms (Fig. 4.5). Sorption of P by soil constituents such as ferric iron and aluminium oxyhydroxides in clay minerals has a major controlling influence in restricting concentrations of bioavailable P (mainly inorganic P) in the soil solution, and on P leaching (Ruttenberg 2001, Reed et al. 2011). Phosphorus is often applied to sugarcane crops in the study areas to supplement the soil's natural P reserves, mainly in the form of organic amendments (e.g., mill mud) and manufactured fertilisers such as diammonium phosphate (DAP) or blends of the two (J. Hughes, pers. comm.).

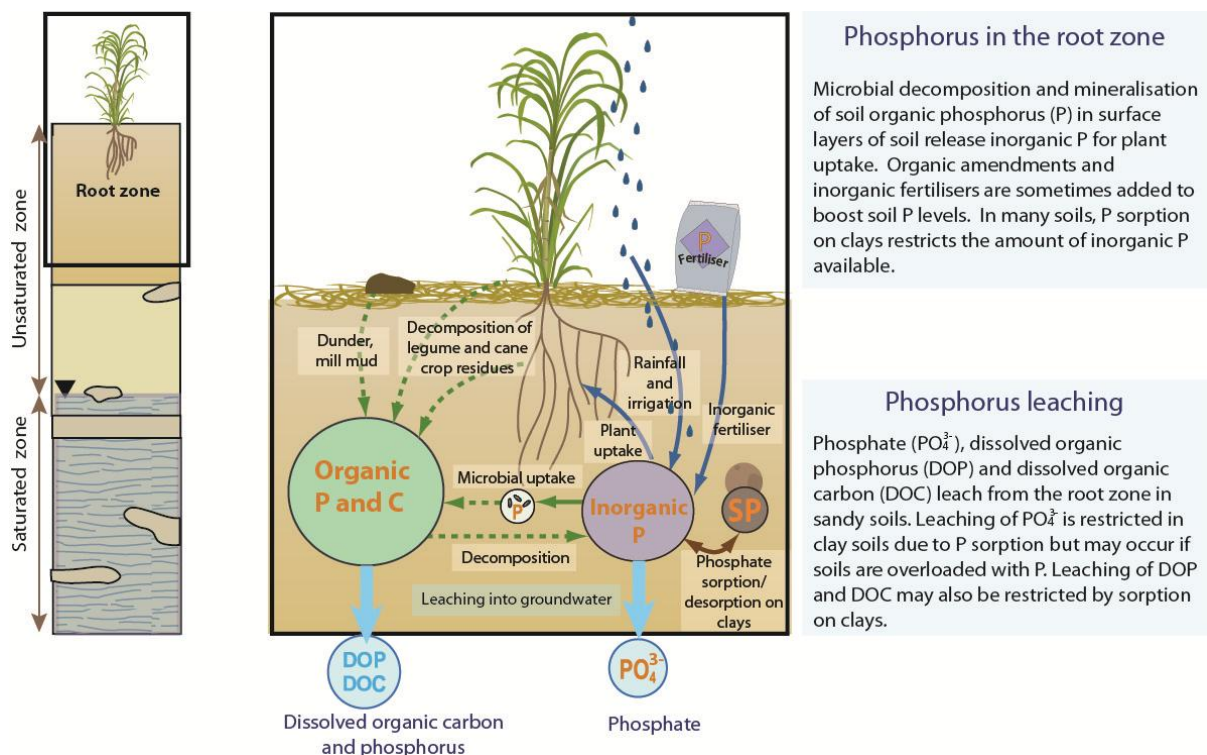


Figure 4.5. Conceptualisation of phosphorus dynamics in the root zone under cane. Adapted from Reed et al. (2011).

Phosphorus transformation and attenuation

Inorganic P and some organic forms of P are susceptible to sorption (Reed et al. 2011), which restricts the extent of their leaching and deep drainage in most soils, the main exceptions being soils with limited sorption capacity (e.g., soils with very low clay content and sands) and soils that have been overloaded with P (e.g., from applications of fertiliser or organic wastes). Natural P sources in groundwater may occur as a result of leaching from overlying soil layers, weathering processes within the aquifer, microbial decomposition of buried marine sediments, and release from naturally occurring iron oxides under anaerobic conditions (Ruttenberg 2001, Slomp and Van Cappellen 2004). Highest P concentrations are typically found in shallow groundwater associated with agricultural lands or wastewater plumes (e.g., from on-site septic systems) (Slomp and Van Cappellen 2004). Key processes and pathways that influence the fate of P in subsurface environments below the root zone are summarised in Fig. 4.6.

In general, under aerobic conditions dissolved P in groundwater is readily removed through sorption or precipitation processes (Fig. 4.6), but P may be mobile in aquifers exposed to excessive P loadings: inorganic P removal is considered less efficient under anaerobic conditions and occurs mainly through precipitation of calcium or iron phosphate (Slomp and Van Cappellen 2004). Depending on

prevailing conditions in transition zone between aerobic/anaerobic fresh groundwater and aerobic/anaerobic seawater, the potential transformations of P that may occur encompass the suite of reactions shown in Fig. 4.6; e.g., as shown in Fig. 4.7 for one possible scenario. The more ready attenuation of P relative to N can result in significant increases in the inorganic N/P ratio along groundwater flow paths which could have important implications for ecosystem processes in receiving surface waters (Slomp and Van Cappellen 2004). These authors reviewed P flux rates via SGD and found daily rates as high as 13 mg P/m²/d reported from an alluvial aquifer in southern Chesapeake Bay and 29 mg P/m²/d from an anaerobic aquifer in South Carolina.

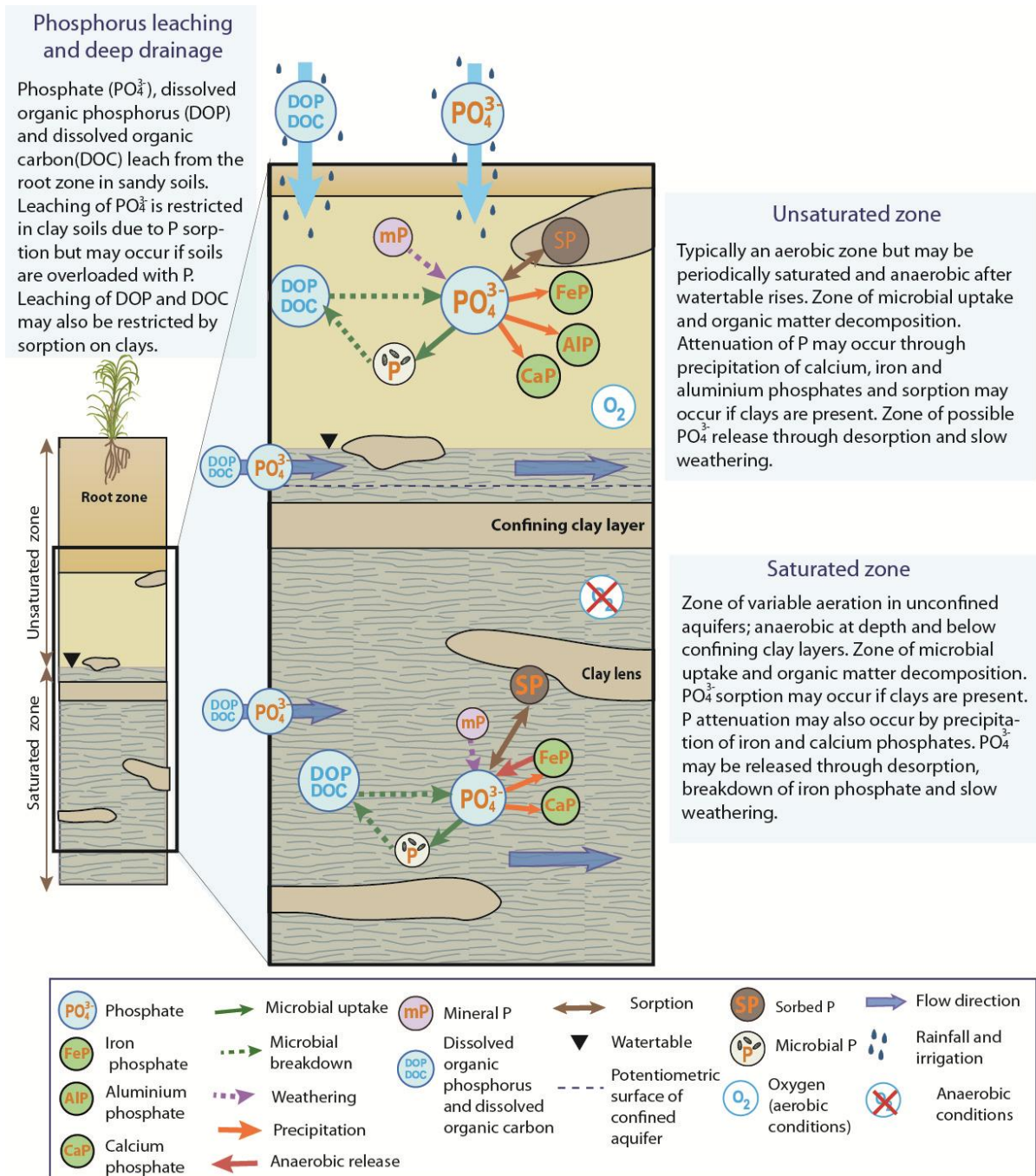


Figure 4.6. Conceptualisation of processes involved in the subsurface transport, transformation and attenuation of phosphorus in the unsaturated and saturated zones.

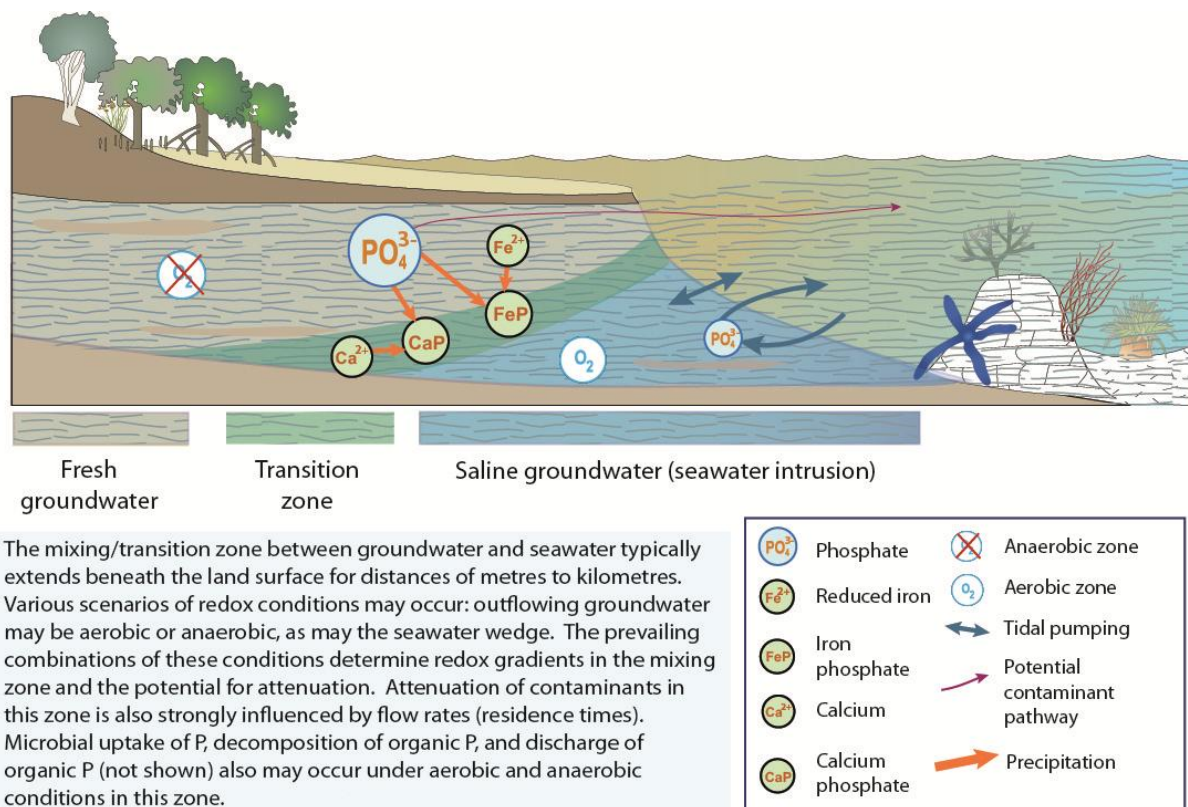


Figure 4.7. Conceptualisation of one scenario of potential phosphorus attenuation processes in the transition zone, in which anaerobic fresh groundwater mixes with intruding aerobic seawater. Adapted from Slomp and Van Capellen (2004).

Studies in Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas

The review found very few reports from the study areas on P transport, transformation or attenuation in subsurface environments beneath the root zone. The two exceptions below were both conducted in the Wet Tropics.

In the Johnstone catchment, a study of the P mass-balances of plant and ratoon crops of bananas and sugarcane found leaching losses of P below 60 cm were negligible (Moody et al. 1996). This result was not unexpected, given the strongly P-sorbing Ferrosol soils on which the crops were grown. By contrast however, monitoring of 24 bores in the Johnstone found inorganic P (FRP) to be present in groundwater, at median concentrations in the range 0.005–0.22 mg P/L (Rasiah et al. 2011). Similarly, in the Tully catchment, inorganic P was found in both groundwater (up to 0.16 mg P/L) and drains (up to 0.11 mg P/L). Organic P was also present in samples from both catchments and comprised on average 38% of the total dissolved P (Rasiah et al. 2011). These levels of P in groundwater were surprising given the high clay contents of soils in both study areas; as a possible explanation, the authors suggested that P transport into groundwater may have occurred via bypass flow rather than through the soil matrix (Rasiah et al. 2011).

4.3 Herbicides

As noted previously, five PSII herbicides are commonly applied in cane-growing areas of the Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas to control weeds at various stages of the cropping cycle, viz.: ametryn, atrazine, diuron, hexazinone and metribuzin (C. Johnson, pers. comm.), although the use of diuron is currently suspended and under review. In general, the prolonged persistence of herbicides in soil can impair soil health, e.g., through adverse effects on non-target plants, and on soil organisms and microbial processes such as N fixation (Kookana et al. 1998). However specific effects of PSII herbicides on such processes have not been well documented,

particularly for tropical environments where high temperatures, high humidity and intense rainfall may markedly affect their behaviour, thus limiting the applicability of information reported from other climatic regions, even within Australia (Kookana and Simpson 2000).

Herbicide transformation and attenuation

Rainfall and irrigation can mobilise these herbicides in soils, with several studies reporting their presence in surface runoff at paddock, creek and catchment scales (e.g., Davis et al. 2012, Lewis et al. 2009, Smith et al. 2011) and in the GBR lagoon (discussed by Lewis et al. 2009). Rainfall and irrigation can similarly transport these herbicides below the soil surface, where their chemical properties can have a major influence on their fate. Within the root zone they may retain their efficacy for some time and be taken up by plant roots, or they may be subjected to microbial or abiotic degradation into breakdown products that may or may not retain herbicidal properties (Fig. 4.8). To varying extents these herbicides may be sorbed onto soil organic matter or onto clay minerals. Several mechanisms may be involved and this characteristic is commonly described by the sorption coefficients K_d and K_{oc} , with the latter defined as the sorption coefficient (K_d) per unit of soil organic carbon (Kookana and Simpson 2000). There is only limited information available on the sorption properties of PSII herbicides in Australian soils and K_{oc} data derived for soils elsewhere may have limited applicability here, one reason being that K_{oc} depends on the type of organic matter present in a soil as well as the total amount; with pH also a major influence on sorption-desorption of the triazine herbicides (e.g., ametryn, atrazine) (Kookana et al. 1998).

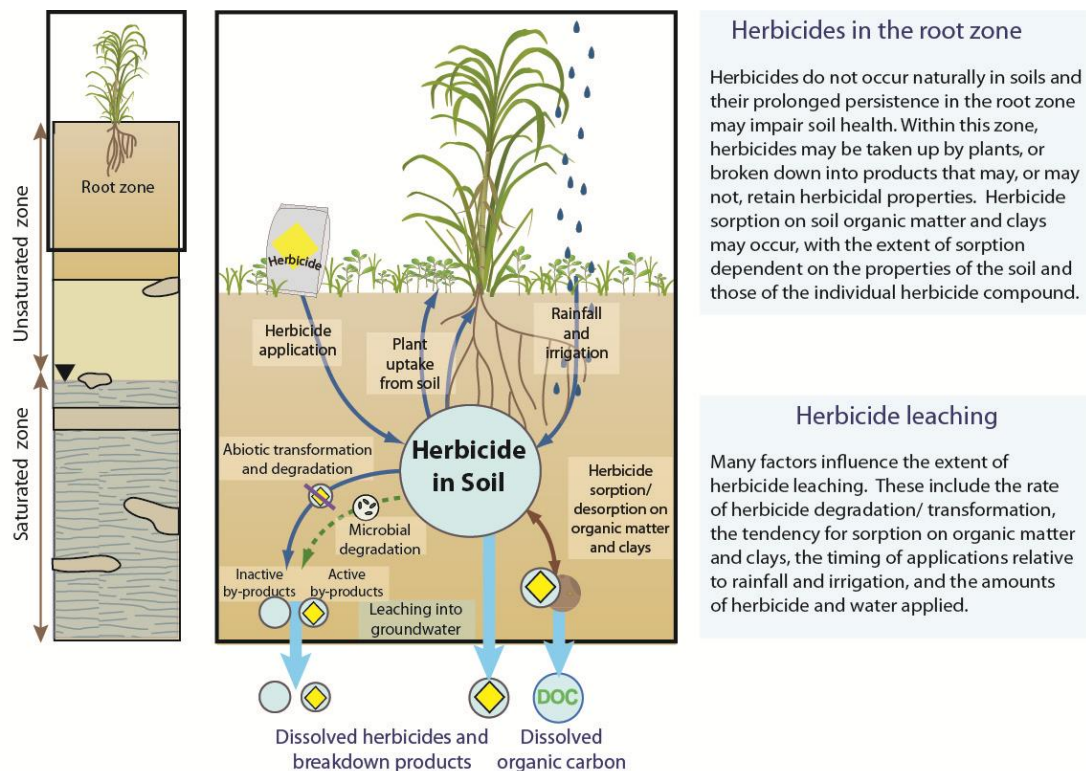


Figure 4.8. Conceptualisation of processes affecting the fate of PSII herbicides in the root zone under cane. Adapted from Kookana et al. (1998).

The persistence of a herbicide in soil is often described by its half-life (the time taken for the soil concentration to be reduced by half under controlled laboratory conditions). However, the time taken for dissipation of 50% of the applied mass (DT_{50}) is sometimes preferred in field environments, to take into account the various potential loss mechanisms that may occur in addition to degradation and transformation (e.g., via runoff, leaching, volatilisation) (Simpson et al. 2001). Half-life and K_{oc} are two important factors that influence the fate of herbicides in soil and the likelihood of their leaching to groundwater. Soil properties, irrigation management, and the rates and timing of herbicide applications relative to rainfall and irrigation, can also have a major bearing on the extent of herbicide

leaching (Kookana et al. 1998). There is some evidence that the risk of leaching may be increased with the adoption of reduced tillage practices due to improved soil structure (Flury 1996, Locke and Bryson 1997) but this is not always the case (Locke and Bryson 1997).

Microbial degradation/transformation is considered the primary mechanism for herbicide loss in soils and sediments, with temperature, moisture content, pH, Eh, and the nature and amount of organic matter present being important influences on rates of loss (Kookana et al. 1998). The retention of crop residues can have variable effects on the rate of herbicide degradation, with no consistent pattern apparent (Locke and Bryson 1997). Microbial degradation rates may be lower in anaerobic subsurface environments when organic matter levels are low and microbial populations sparse (Kookana and Simpson 2000), although abiotic degradation (e.g., hydrolysis, oxidation–reduction) can be an important mechanism in these types of environments (Kookana et al. 1998) (Fig. 4.9).

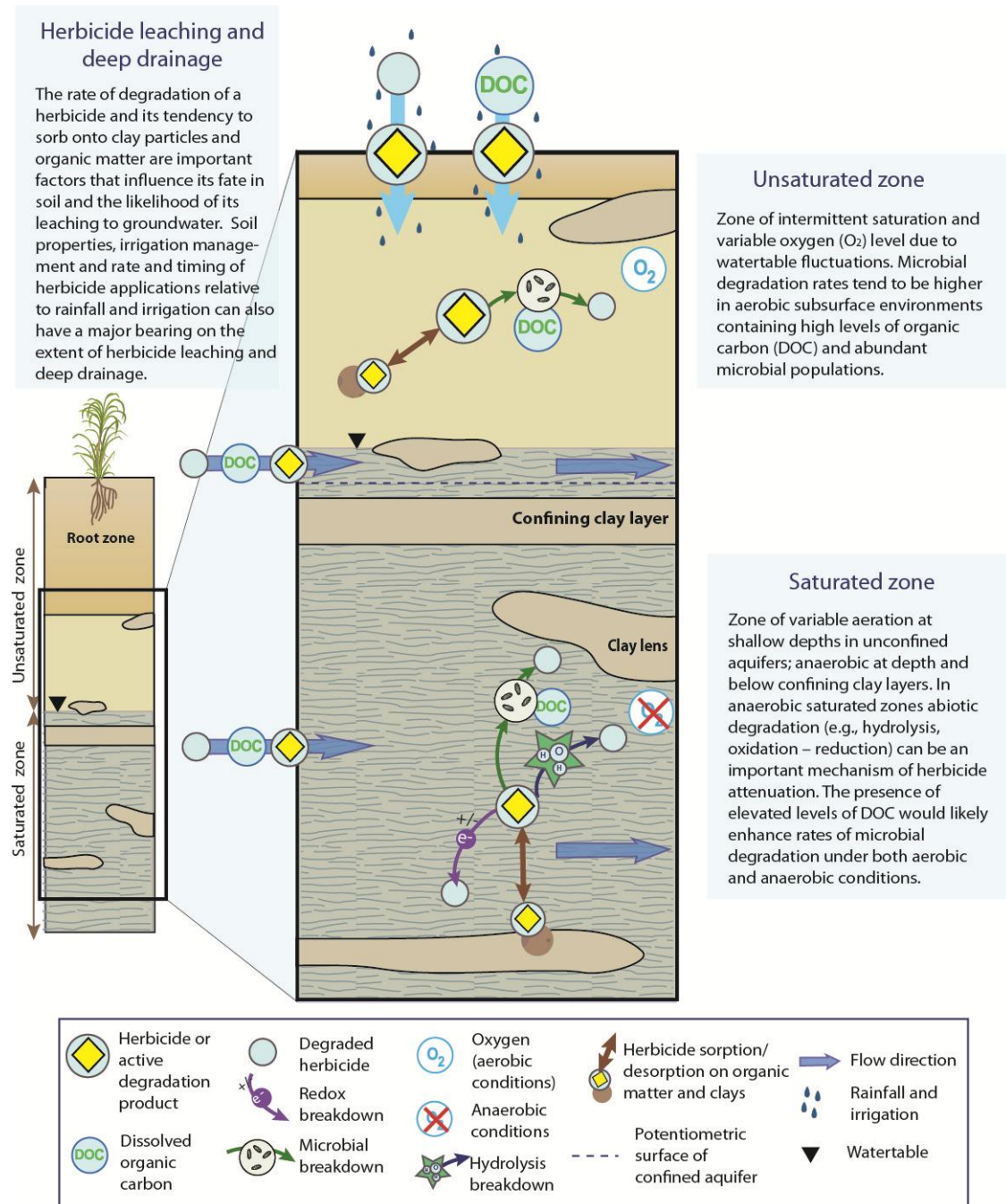


Figure 4.9. Conceptualisation of processes involved in the subsurface transport and attenuation of herbicides in the unsaturated and saturated zones.

The presence of elevated levels of dissolved organic matter generally may be expected to increase rates of microbial degradation under both aerobic and anaerobic conditions. However, the effects may vary depending on the specific type and amount of organic matter present, and any related changes to aquifer microbial communities (Dillon et al. 2009). The degradation products of herbicides sometimes can be as toxic as the parent compounds (Kookana et al. 1998), thus highlighting the importance of monitoring levels of these products as well as those of the parent compounds. For example, two studies in the USA found concentrations in groundwater of degradation products of cyanazine and metolachlor greatly exceeded levels of respective parent herbicides, although this was not always the case for atrazine (Kolpin et al. 1998, Steele et al. 2008). Further, the mobility of degradation products may differ from that of their parent compound; e.g., hydroxyatrazine is much less mobile than atrazine or other atrazine breakdown products (Flury 1996).

Studies in Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas

Apart from the monitoring surveys discussed in Section 3.5, few studies to date have investigated the fate of pesticides in soils and groundwater in the Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas. The study of Simpson et al. (2001) was conducted at cane-growing sites in the southern GBR region (outside the geographic scope of this review) but some of the work is discussed briefly below because of its wider relevance to the GBR region.

Levels of eight pesticides were investigated in soils, irrigation water and soil water of the Burdekin Delta in 2002–2003, including the PSII herbicides ametryn, atrazine, hexazinone and diuron (Klok and Ham 2004). Residues of these herbicides were detected only infrequently and at low to very low concentrations in irrigation water and soil cores (to 1.5 m depth). By contrast, residues were detected at 1.5 m depth in nineteen of 67 soil water samples taken periodically over two irrigation seasons, with diuron the most commonly detected (14 samples, at concentrations up to 0.90 µg/L), followed by atrazine (four samples). Ametryn was not detected in any soil water sample and hexazinone in only one, at low concentration. This ‘snapshot’ study provided useful insights into the potential for these herbicides to move through the soil profile and it highlighted the need for follow-up investigations, including within the aquifer of the Burdekin Delta.

In the Sandy Creek catchment (Mackay–Whitsunday area), levels of hexazinone and diuron were similarly monitored in drainage water at a depth of 0.9 m under cane grown on a deep, self-mulching medium clay soil (Rohde et al. 2011). Residues of both compounds were highest on the first sampling occasion (ten days after application), at around 15 µg/L hexazinone and 8 µg/L diuron; with concentrations of both subsequently showing an exponential decline with time to <2 µg/L after approx. six months. Under these conditions, DT₅₀ in drainage water at 0.9 m depth was 58 and 59 days for diuron and hexazinone, respectively – much greater persistence than the respective DT₅₀ of 11 and 9 days, for residues on the cane-trash blanket. Above-average rainfall two months after application resulted in the formation of a shallow perched watertable (to within 1 m of the soil surface), which persisted for about six months (Rohde et al. 2011); thus highlighting the potential threats to surface water quality, in situations where shallow groundwater discharges rapidly to streams.

A local perched watertable was similarly present under cane grown on a free-draining Dermosol soil on a gentle slope near Bundaberg in the southern GBR region, due to restricted subsurface drainage down-slope. Monthly groundwater sampling in a network of piezometers (to 3.5 m depth) over three wet seasons revealed variable concentrations of atrazine and diuron in groundwater, at concentrations up to approx. 8 µg/L atrazine and 6.5 µg/L diuron (Simpson et al. 2001). Despite the moderate sorption capacity of diuron in soil, its presence in groundwater was considered indicative of its transport by preferential flow paths such as those formed by old root channels or cracks (i.e., bypass flow). The groundwater discharged to an adjacent small creek so that residence times would likely have been relatively short, providing limited time for herbicide degradation and attenuation prior to discharge.

4.4 Links to on-farm management

Sugarcane is by far the dominant crop grown in coastal parts of the Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas (Figs. 1.1–1.3). Production systems vary widely across these areas due to the broad range of environments in which cane is grown, including differences in climate, topography and soil type. In general, best-practice guidelines for the cane industry recognise the importance of minimising risks of groundwater contamination in the advice they provide on fertiliser, herbicide and irrigation management, and management of subsurface drainage (Calcino et al. 2008, Schroeder et al. 2009, Hurney et al. 2008). Similar general principles would apply also to management of horticultural crops in the three areas. Appendix 2 (Tables A2.1, A2.2) outlines some specific principles of nutrient and herbicide management of cane crops that may help minimise risks to groundwater quality, and identifies several current gaps/barriers to improving management practices.

Previous discussion (Sections 4.1–4.3) has summarised the processes and pathways that influence leaching and deep drainage of N, P and PSII herbicides from the crop root zone, while research conducted in the study areas has confirmed the presence of these contaminants in deep subsurface environments (including groundwater) and in shallow groundwater drains. At a farm scale, cropping systems models (e.g., APSIM, McCown et al. 1996) provide a valuable means of integrating the many factors involved in examining linkages between agrichemical and irrigation management, crop yields, climate variability and off-farm losses. Such comprehensive analysis is generally beyond the capabilities of experimental research and monitoring alone. Results from several APSIM modelling applications in the study areas have emphasised the importance of N fertiliser management (and to a lesser extent, irrigation management) in minimising deep drainage losses of N, particularly for the plant-cane crop (Stewart et al. 2006, Thorburn et al. 2011a, Biggs et al. 2012).

Average application rates of N and P fertilisers (kg/ha) across the study areas have declined considerably since the mid-1990s (Incitec Pivot 2009) but further reductions in fertiliser use may be achievable without loss of yield. For example, a recent project in the lower Burdekin aimed to raise awareness among cane-growers of nitrate levels in groundwater and the potential for this to be used as a resource to partially offset other N inputs (e.g., fertiliser), without forgoing yield (BBIFMAC 2012).

Ideally, N fertiliser inputs should be based on a realistic ‘block target yield’ approach which encapsulates the best principles of N management for both Reef water quality and profitability outcomes. The ‘Nitrogen replacement’ (Thorburn et al. 2011b) and ‘Six-easy-steps’ (Schroeder et al. 2009) approaches are both variants of a target yield approach: N-replacement aims to replace the amount of N removed in the previous year’s crop, while Six-easy-steps aims for the district yield potential. Encouraging results have been achieved in trials of both of these approaches, including in some instances using N-replacement, a potential reduction in environmental N losses of up to 50% (based on N mass balance estimates) without loss of yield, (Thorburn et al. 2011b). However, further work is required to quantify the environmental benefits of these block target yield approaches and demonstrate that they can be achieved with no net loss of economic returns to growers. As well as an evaluation of their long-term economic sustainability, research is needed on optimising the setting of target yields; quantifying N losses via different pathways (e.g., deep drainage and surface runoff); and defining the soil and crop N cycling processes that underpin their performance.

Recent research suggests that sugarcane plants have a strong preference for ammonium rather than nitrate as a source of N (Robinson et al. 2011). This requires further investigation (including field studies) but the results suggest that retaining applied N in the form of ammonium would benefit plant uptake as well as reduce risks of nitrate leaching. There has been little adoption by the cane industry so far of nitrification inhibitors and urease inhibitors. Both types of product have the potential to improve crop fertiliser use efficiency and reduce off-site losses of N; the former by slowing the conversion of ammonium to nitrate (thereby reducing the risk of N leaching) and the latter by slowing down the conversion of urea to ammonium (thus regulating the release of ammonium for plant uptake and reducing volatilisation losses) (Chen et al. 2008). However, evaluation of the potential benefits (and costs) of these products in reducing offsite losses of N should also take into account any adverse environmental effects that may arise from their use. Current research is investigating the efficacy of

nitrification inhibitors and controlled release N fertilisers on N fertiliser use efficiency of cane, on representative soils in the Burdekin and Herbert catchments (P. Moody, pers. comm.).

A survey of the P fertility status of soils in the entire GBR region by Rayment and Bloesch (2006) revealed that 84% of 105 cane-growing sites sampled had excessive levels of P and only 3% of soils were P deficient. (Twenty-two of the sites were located south of the areas covered by the present review, but these tended to have lower soil P levels than sites further north.) The authors concluded that in general, P inputs to cane-lands could be reduced industry wide without a loss in yield and they estimated it would take years to deplete currently elevated soil P levels. They recommended greater use be made of soil test results in decision-making on crop fertiliser P needs and also advocated caution in the use of mill mud and mill ash by-products.

Mill mud and ash are used throughout the study areas on properties within an approx. 20 km radius of a mill (Kanduri 2010). Dunder applications range from 75% of farms in the Sarina district, to 60% in the Mackay district, 20% in the Proserpine district, and 17% in the lower Burdekin (heavy clay soils only), but it is not used in the Wet Tropics (D. Henderson, pers. comm.). Mill ash has high P and potassium contents, while dunder is enriched with potassium (Calcino et al. 2008).

The nutrient content of mill mud can vary substantially over a crushing season and the variability at any one mill may be as great as the variability between mills: on average, application of mill mud at 150 wet tonnes/ha applies about 550 kg total N/ha and 340 kg total P/ha (Bloesch and Barry 2010). The typical ratio (by weight) of total N to total P in mill mud is around 1.6, which means that compared with the ratio in cane (N/P ratios in tops and trash of approx. 6.5) it is highly enriched with P relative to crop needs, assuming the N and P in mill mud are potentially bioavailable (Bloesch and Barry 2010). Furthermore, it can be difficult to accurately estimate the amounts of N and P applied via mill mud because of the variable product content and the difficulties of applying it uniformly, due to its high moisture content. From a groundwater protection perspective, it can be questioned whether mill mud should be applied at all to high P soils, even as a source of N. Potential approaches to reducing the amount of mill mud produced and to improving its transportability and ease of handling were reviewed by Kanduri (2010).

Both dunder and mill mud have high organic matter contents. Mill mud contains around 25% organic C (on a dry weight basis), with an application to soil of 150 wet tonnes (75% moisture content) contributing 8–11 t/ha of organic C (Bloesch and Barry 2010). However, the bioavailability of the applied C and its potential effects on microbial processes in soils and aquifer sediments remain unclear (Bloesch and Barry 2010). In general, bioavailable forms of organic C may affect groundwater quality by stimulating microbial growth and activity, which in turn may enhance transformations and attenuation of nutrients and herbicides (NRMMC, EPHC & NHMRC 2009). The increased microbial activity may be accompanied by changes to the structure and function of aquifer microbial communities (Dillon et al. 2009). Other potential effects of DOC inputs include clogging of aquifer pore spaces; and a reduction in groundwater redox potential, with associated increases in levels of some inorganic ions (e.g., arsenic, Fe^{2+}) (NRMMC, EPHC & NHMRC 2009). Furthermore, for nitrate, very high levels of bioavailable C may favour the DNRA process instead of denitrification (Section 4.1) and so retain N within the subsurface zone. Research is now in progress to assess the rate of release of bioavailable C, N and P from mill by-products (P. Moody, pers. comm.).

Limiting the extent of deep drainage is critical to restricting contaminant transport to groundwater and in managing rising groundwater levels and subsequent increased discharge potential. Improved irrigation management has the potential not only to increase water use efficiency and the profitability of sugarcane production (Schroeder et al. 2009), but also to reduce risks of deep drainage and groundwater contamination. This is particularly the case in managing the timing of irrigation relative to fertiliser and herbicide applications. On an annual basis however, drainage is likely to be dominated by major rainfall events during the wet season (e.g., cyclones), when any effects of management practices would likely be minimal. As noted previously, the likely benefits of improved irrigation management are now being assessed as a potential mitigation approach in areas of the lower Burdekin affected by rising groundwater levels (Bennett 2012).

4.5 Summary of key points

- Leaching and deep drainage of N occurs mainly as nitrate and to a lesser extent dissolved organic N; leaching of ammonium occurs only in sandy soils or in soils overloaded with ammonium
- Denitrification is the primary mechanism for removing N from aquifers and groundwater/surface water transition zones; it relies on the presence of dissolved organic carbon (DOC) or another source of electrons; ammonium, if present, may be detained on cation exchange sites on clays
- Leaching and deep drainage of P is restricted by P sorption on clays, but leaching of inorganic and organic P may occur in sandy soils, or if soils are saturated with P; levels of P in groundwater may be attenuated through precipitation and sorption on clays, although P may sometimes be released back into solution by desorption or other mechanisms
- Typically, the potential for attenuation of P in aquifers tends to be greater than that of N, which may cause N:P ratios to increase along groundwater flow paths, with implications for ecosystem processes in surface waters in areas of groundwater discharge
- PSII herbicides may retain their efficacy in the root zone for some time, or they may be subjected to microbial or abiotic degradation; their chemical properties have a major influence on their sorption onto soil organic matter or clay minerals (and thus the extent of leaching), but only limited information is available on the sorption properties of PSII herbicides in Australian soils
- Soil properties, irrigation management, the amount of herbicide applied and the timing of applications relative to rainfall/irrigation also have a major bearing on the extent of leaching; microbial degradation/transformation is the main mechanism for herbicide attenuation in aquifers, while abiotic degradation may be important in anaerobic environments
- Overall, key determinants of the fluxes of N, P and PSII herbicides through aquifers to streams and coastal waters are: the supply rate of these contaminants from the soil surface via deep drainage, redox conditions in subsurface environments, the residence time of groundwater within aquifers, the extent of contact with clay sediments, and the availability of DOC (or in the case of denitrification, alternative sources of electrons)
- Research in cane-growing areas of the Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas has confirmed the presence of N (as nitrate) in deep subsurface environments and shallow groundwater drains; however, there have been relatively few studies of P and PSII herbicides in these environments
- In the Johnstone catchment, an average of 1,550 kg nitrate-N /ha is temporarily held on anion exchange sites deep in the profile of Red Ferrosol soils under cane, with the potential for this to be slowly released via deep drainage over a period of decades; the extent to which this situation exists in other agricultural soils of the Wet Tropics is not known
- Enhanced N fertiliser management is a key strategy for minimising deep drainage losses of N, with the ‘block target yield’ approach offering the potential to fine-tune N application rates while maintaining yields
- Current research is investigating the potential for ammonium-based fertilisers to improve N-use-efficiency by cane and reduce off-site N losses, when used in combination with inhibitors of urease activity and nitrification
- Most cane-growing soils in the Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas have a high P fertility status and do not require the addition of P fertiliser or organic amendments enriched with P (e.g., mill mud).

5. Groundwater Fluxes of Nutrients and Herbicides to the Reef Lagoon

5.1. Overview

As discussed in preceding sections of the report, many factors influence the transport, transformation and attenuation of N, P and PSII herbicides in soils and deeper subsurface environments, and their potential discharge via groundwater pathways to the Reef lagoon. Important elements of these processes and pathways are summarised in Fig. 5.1. As noted previously, the risk of contamination as a result of anthropogenic activities (e.g., land use and land management practices) is likely to be much greater for shallow, unconfined aquifers with relatively high rates of groundwater recharge, than for confined aquifers at considerable depth (Winter et al. 1998, Slomp and Van Cappellen 2004). Shallow, unconfined aquifers are thus likely to represent the dominant pathways for contaminant discharge to the Reef lagoon. Nevertheless, as shown in Fig. 5.1, relatively deep, confined aquifers may also represent a possible pathway for discharge of some contaminants; e.g., nutrients derived from decomposition of buried marine deposits of organic matter.

The following sections of the report address two key questions arising from a synthesis of the information assessed in the review:

- i. How important are groundwater fluxes of contaminants relative to surface water fluxes?
- ii. What are the implications for catchment-to-reef scale monitoring of contaminant fluxes?

5.2. Receiving environments of groundwater discharge

Discharge to rivers, wetlands and estuaries

As shown in Fig. 5.1, riverine and wetland environments in some settings can have an important role in removing contaminants from inflowing waters, thus helping to protect the health of aquatic ecosystems downstream (e.g., Hill 1996, Mitsch and Gosselink 2000). Riparian and wetland vegetation has been cleared in many parts of the Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas since European settlement (Russell and Hales 1996, Johnson et al. 1999), with the rehabilitation and conservation of remaining areas targeted as one of the Reef Plan’s key objectives (The State of Queensland 2009a). Care is required in utilising the buffering capabilities of such areas to ensure their inherent resilience is protected, since excessive stress may not only impair their capacity to remove contaminants, it may also put at risk their other functions and values (O’Keeffe and Schofield 2001, Wetzel 2001, Swift et al. 1998).

Acid sulfate soils (ASS) are a feature of many coastal wetland landscapes in the Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas, with the ASS layers often found close to the surface in conjunction with shallow, fluctuating watertables (Powell and Martens 2005). Where ASS are retained in their natural state (i.e., not drained), the iron sulphides and other sulfidic materials they contain provide a potential source of reduced iron (Fe^{2+}) and sulfur (S^{2-}). As discussed in Sections 4.1 and 4.2, both Fe^{2+} and S^{2-} can facilitate the attenuation of N in groundwater via denitrification, while Fe^{2+} provides a mechanism for attenuation of P through precipitation of iron phosphate. Drainage of ASS (e.g., for agricultural or urban development) can lead to serious acidification problems in estuaries and other surface waters, due to the oxidation of these sulfidic compounds and the formation of sulphuric acid (de Weys et al. 2011, Powell and Martens 2005). The acidification is exacerbated by the associated dissolution of aluminium and heavy metals, which may have serious impacts on ecosystems in receiving waters, and in extreme cases cause disease or death of affected organisms (Powell and Martens 2005). Drainage from areas of ASS has also been implicated in the occurrence of harmful blooms of *Lyngbya majuscula* in marine waters (including near islands and bays of the GBR), although the exact nature of the links between ASS drainage and outbreaks of blooms remains to be clarified (Powell and Martens 2005). These effects of ASS drainage may be compounded by the presence in drainage waters of other contaminants, such as herbicides.

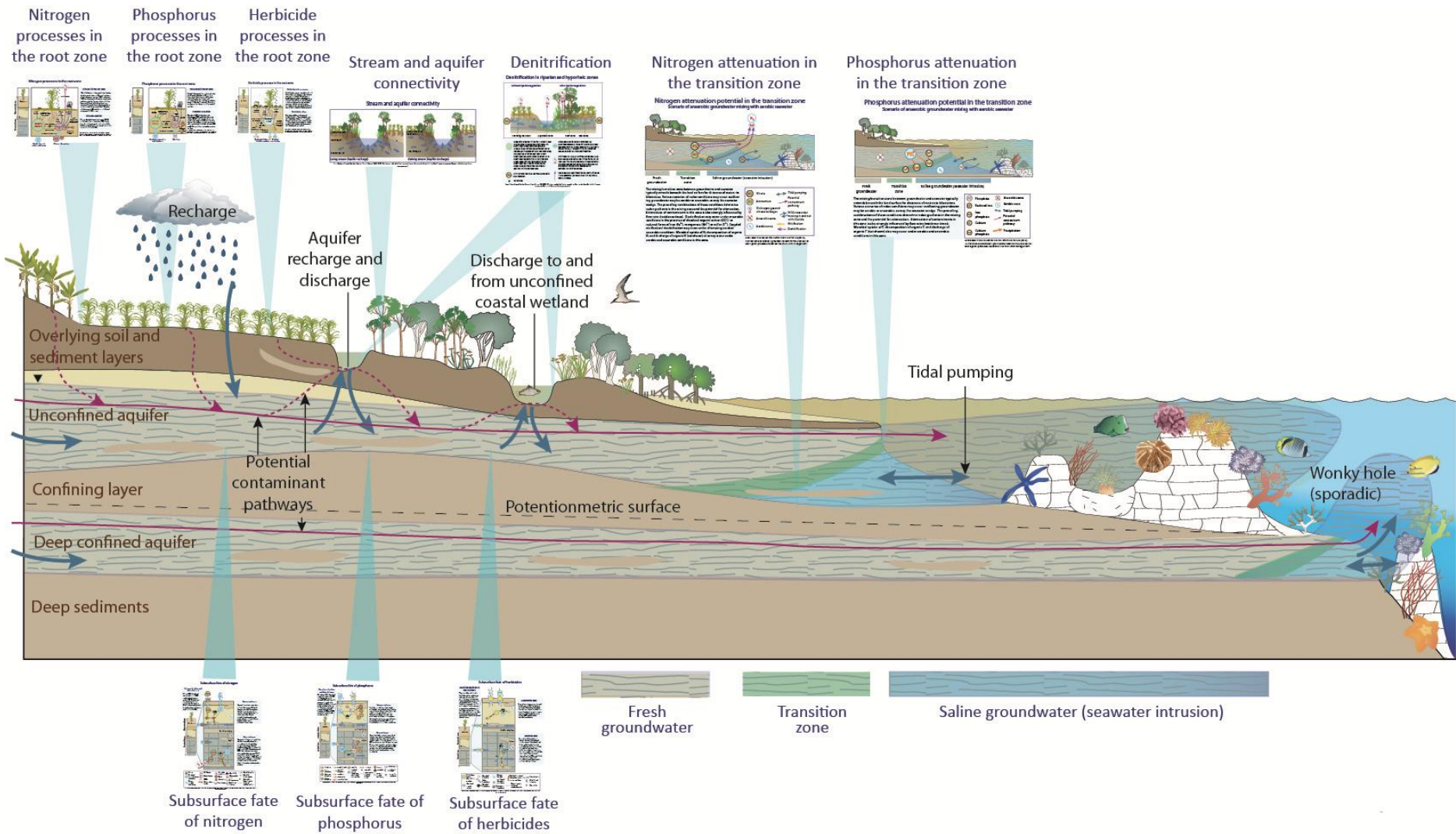


Figure 5.1. Overview of key pathways and processes involved in the leaching and deep drainage of nutrients and herbicides to groundwater, their fate in the root zone and deeper subsurface environments, and their discharge to surface water receiving environments.

In general, little information is available on specific riverine and wetland areas that receive groundwater discharge in the Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas, a notable exception being rivers and streams in the lower Burdekin (Cook et al. 2004, 2011). Nevertheless, in broad terms, middle and lower sections of rivers in the Wet Tropics have been identified as receiving groundwater discharge, with shallow groundwater discharge to streams and drains also common in this area, as well as in the Mackay–Whitsunday area (discussed in Section 5.4).

Useful guidance on specific areas of groundwater discharge could be obtained by mapping the surface elevation of groundwater from as many observation and private bores as possible, including short term responses in the wet season and the variation in levels throughout the year (R. Shaw, pers. comm.). This would help identify whether flows are directly to the coast or to streams, and would provide a rough estimate of fluxes. Mapping of groundwater-dependent ecosystems across the study areas, as currently being investigated in two selected areas of the state (The State of Queensland and Commonwealth of Australia 2011), would also assist greatly in understanding patterns of groundwater discharge. Further, it would allow identification of ecosystems at risk of exposure to contaminants in groundwater, and would enable assessment of their potential for mitigating contaminant loads. It would also highlight areas in need of conservation and/or remediation.

Discharge to coastal environments

Groundwater discharge via confined submarine aquifers (‘wonky holes’) has been documented up to 10 km offshore from most rivers of the central and northern GBR lagoon (Stieglitz 2005) but its occurrence is sporadic. Muddy shorelines, sandy beaches and estuaries characterise much of the coastline of the GBR region, including the Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas. They comprise an inter-linked mosaic of mangrove, salt marsh, freshwater wetland, seagrass beds and other habitats of extraordinary biodiversity which are of fundamental importance to ecosystem health and processes more widely in the Reef lagoon (Sheaves et al. 2007, Lovelock and Ellison 2007). The nature and extent of the dependency of these ecosystems on groundwater has not yet been well described or mapped, but information from elsewhere would suggest that across these coastal and marine ecosystems, it is likely the degree of dependency may range from some that are entirely dependent, or highly dependent on groundwater, to others that may be only partially dependent, or not dependent at all (Hatton and Evans 1998, Sinclair Knight Merz 2005, Froend et al. 2004). Associated with this dependency would be the potential threat of exposure to any contaminants in the groundwater discharged, although there may also be beneficial effects (e.g., from nutrients).

Widespread areas of submarine groundwater discharge have been mapped along the coastline and in estuaries of the Wet Tropics and the lower Burdekin (Stieglitz et al. 2010), but to date there has no similar mapping conducted along the coast of the Mackay–Whitsunday area. The mapping has highlighted the ubiquitous presence of groundwater discharge and the potential risks to critical ecosystems from exposure to nutrients and herbicides in the groundwater discharged. For example, in the lower Burdekin there is considerable groundwater discharge to the extensive wetlands of Bowling Green Bay (Cook et al. 2011), which are recognized under the Ramsar Convention as being of international significance. This emphasises the importance of mitigating contaminant loads in groundwater, if critical coastal ecosystems such as these are to be protected.

Temporal patterns of groundwater discharge

The temporal patterns of groundwater discharge are an important factor in assessing the overall significance of contaminant discharge via groundwater pathways relative to surface water transport. Whereas contaminant discharges from rivers to the coast are strongly dominated by major episodic events during the wet season, the slower response of groundwater discharge via regional aquifers extends the potential exposure period of coastal ecosystems in receiving waters well into the dry season, and possibly to all year round (Stieglitz 2005). Furthermore, this exposure may be exacerbated by differing seasonal patterns of water circulation in the Reef lagoon. River flood-plumes typically spread longshore northward from river mouths for tens of kilometres or more, before spreading seaward and dissipating over a period of days to weeks, or in the case of major flooding in the Burdekin and Fitzroy river systems, possibly months (Brodie et al. 2012). By contrast, circulation

patterns in the dry season often result in the formation of a coastal boundary zone, which traps shallow near-shore waters (including those receiving groundwater discharge) and restricts the extent of mixing and dilution with better quality waters further off-shore (Alongi and McKinnon 2005).

Groundwater discharge to rivers may often occur relatively rapidly (e.g., shallow discharge to drains), with groundwater-borne contaminants potentially entrained in receding flood-waters. However, groundwater discharge to rivers may be much slower where flow paths are deeper and longer and thus may occur during periods of relatively low stream flow, when river discharge is more likely to be distributed much closer to the coast (as noted above). For example, in the Johnstone catchment, >90% of the mean annual flux of suspended sediment was estimated to occur in the highest 10% of daily flows (i.e., during major to moderate flood events) but only 51%–58% of the annual fluxes of nitrate and dissolved forms of P occurred at these times (Hunter and Walton 2008), which is consistent with a greater involvement of subsurface transport processes in the fluxes of these contaminants and their transport to the Reef lagoon during periods of relatively low flow.

5.3. Hypothetical estimates of groundwater contaminant fluxes

Although there have been relatively few groundwater monitoring studies of nutrients and herbicides (apart from nitrate), it is clear that one or more of these contaminants has been found in groundwater in various parts of the Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas, sometimes at concentrations that may have posed a threat to ecosystems in receiving waters, if discharged at the concentrations reported. The review found no information on contaminant concentrations or fluxes measured in receiving environments at the point of actual discharge, whether directly to the coast or to riverine environments (apart from limited studies of fluxes to drains).

To gain a broad indication of the possible significance of groundwater pathways in the transport of contaminants to the Reef lagoon, comparisons were made between hypothetical estimates of loads discharged by groundwater pathways and mean annual loads discharged to the Reef lagoon by rivers (Table 5.1). The main purpose in making the comparisons was to gain an initial sense of the potential significance of groundwater loads relative to river loads, on an orders-of-magnitude scale. Given the unavailability of groundwater data on contaminant concentrations and fluxes as noted above, the data presented in Table 5.1 should be treated with considerable caution due to their high levels of uncertainty. The areas selected for comparison were those where data were available on contaminants in groundwater, while the chosen concentrations (of nitrate and total dissolved P) were indicative of respective median or mean values reported in the literature (Sections 3.2 and 3.3).

Estimates of PSII herbicide loads were not included in Table 5.1, since median values for these areas were below respective limits of detection, taking into account the proportion of samples in which positive detections were not recorded (studies of Hunter et al. 2001, Baskaran et al. 2002, Budd et al. 2002 and Shaw et al. 2012). Moreover, in terms of potential impacts of herbicides, concentrations rather than loads may be the more relevant indicators of risk, particularly to ecosystems in the immediate receiving environments.

It should also be noted that while the river flux estimates of Kroon et al. (2011) were for dissolved inorganic N (ammonium-N and nitrate-N combined), the hypothetical groundwater flux estimates in Table 5.1 were for nitrate only. The extent to which any ammonium in groundwater would be discharged to surface waters remains unclear; limited data for groundwater from the Johnstone and Pioneer Valley aquifers suggest concentrations in groundwater are generally low (e.g., median level of around 0.01 mg N/L, Section 3.3). However, the presence of ammonium in groundwater at concentrations up to 4 mg N/L in some parts of the lower Burdekin aquifer (Thayalakumaran et al. 2008, Lenahan 2012) indicates that the potential for groundwater discharge of ammonium should not be discounted. Periodic monitoring of ammonium levels in groundwater would therefore be warranted. It is likely any ammonium discharged would rapidly be converted to nitrate in aerobic receiving waters (Figs. 4.2, 4.4).

Despite the limitations of the data presented in Table 5.1, they nevertheless indicate there is potential for relatively small but significant amounts of nitrate and P to be transported to the Reef lagoon by groundwater in each of the selected areas. By these calculations, groundwater fluxes of both nitrate and P to rivers and the coast of the lower Burdekin would far exceed the corresponding groundwater fluxes of these contaminants to rivers and the coast in the Johnstone and Pioneer (Table 5.1).

Table 5.1. Hypothetical loads of nitrate and total dissolved phosphorus discharged annually from the Pioneer Valley, lower Burdekin and lower Johnstone aquifers and comparisons with corresponding mean annual loads discharged by rivers¹

	Pioneer	Burdekin	Johnstone
<u>Hypothetical groundwater concentration^{2,3}</u>			
Nitrate-N (mg N/L)	1.0	2.0	0.3
<i>Reported range (mg nitrate-N/L)</i>	<i>(<0.0–20)</i>	<i>(<0.01–39)</i>	<i>(<0.0–5)</i>
Total dissolved P (mg P/L)	0.1	0.15	0.03
<i>Reported range (mg P/L)</i>	<i>(0.0–0.8)</i>	<i>(0.01–0.6)</i>	<i>(<0.02–0.3)</i>
<u>Groundwater loads to coast⁴</u>			
Nitrate-N (t N/y)	16	190 (25) ⁵	1
Total dissolved P (t P/y)	1.6	14 (2)	0.1
<u>Groundwater loads to rivers^{4,6}</u>			
Nitrate-N (t N/y)	22	323	87
Total dissolved P (t P/y)	2.2	24	9
<u>Mean annual river loads to the Reef lagoon⁷</u>			
Dissolved inorganic N (t N/y) ⁸	280	1,800	2,100
Total dissolved P (t P/y)	161	314	110
<u>Combined groundwater loads⁹ as a proportion of mean annual river loads</u>			
Nitrate-N (%)	14	28	4
Total dissolved P (%)	2.4	12	9

¹Note that no account has been taken of possible contaminant attenuation in groundwater prior to discharge, which potentially could reduce nitrate and P concentrations to negligible levels; ²Rounded approximations of median groundwater concentrations for: Pioneer nitrate and TDP (Baskaran et al. 2002, Budd et al. 2002); Burdekin nitrate 1990–2005 (Barnes et al. 2005), TDP (Budd et al. 2002); Johnstone nitrate and TDP (Hunter et al. 2001); ³Concentrations italicised in brackets are min./max. ranges reported in the above studies; ⁴Estimated using discharge data from Table 2.1; ⁵Values italicised in brackets for the lower Burdekin are N and P loads calculated using discharge data of McMahon et al. (2012) instead of Cook et al.'s (2011) data – see Table 2.1; ⁶For the Burdekin, includes discharge to the Burdekin R., Haughton R., Barratta Ck.; ⁷From Kroon et al. (2011), Table 5; ⁸Nitrate-N+ammonium-N); ⁹Groundwater loads to rivers + groundwater loads to the coast.

It is important to acknowledge that the approach used in Table 5.1 takes no account of nutrient attenuation in groundwater prior to discharge (as discussed in Sections 4.1 and 4.2) which potentially could reduce concentrations and loads to negligible levels. For example, in the lower Burdekin, while nitrate concentrations in groundwater are relatively high at some locations and the overall mean concentration since 1990 is around 2 mg nitrate-N/L (Barnes et al. 2005), concentrations are very low near the coast of Bowling Green Bay, where geochemical conditions are supportive of attenuation via denitrification (Thayalakumaran et al. 2008, Lenahan 2012). On the other hand, pockets of relatively high nitrate concentrations exist in groundwater near Home Hill and close to the Coral Sea coast (Thayalakumaran et al. 2008, Lenahan 2012).

Note also that the annual groundwater discharge estimates from the lower Burdekin aquifer used in Table 5.1 were extrapolated from daily measurements made at the end of the wet season, and may therefore represent the high end of groundwater flow rates, particularly those to rivers: moreover, considerable uncertainty was inherent in these daily discharge estimates (Cook et al. 2011). By comparison, the hypothetical groundwater fluxes of nitrate-N and P to the Burdekin coast would be only approx. one-seventh those calculated using Cook et al.'s 2011 data, if they were based instead on long-term mean annual discharge data for the period 1981–2006 (McMahon et al. 2012) (Table 5.1).

Furthermore, the hypothetical estimate that only 4% of the total nitrate discharged from the Johnstone was sourced from groundwater (Table 5.1) would seem inconsistent with results of previous research that suggested a much greater role of groundwater processes in the transport of nitrate in that catchment (Hunter and Walton 2008, Walton and Hunter 2009). A possible explanation may be the contribution to groundwater discharge from nitrate held on anion exchange sites in the soil profile (as discussed in Section 4.1), which may not be reflected in groundwater nitrate concentrations measured in monitoring bores, except possibly during the wet season. In addition, it is likely the estimate of the annual river flux of nitrate from the Johnstone River system (Table 5.1) would also include a considerable proportion of the groundwater flux (i.e., that discharged upstream of the end-of-system river monitoring site, Section 5.4); hence it would be an over-estimate of the magnitude of the flux derived strictly via surface water processes.

These examples for the lower Burdekin and the Johnstone illustrate the very high degree of uncertainty concerning current knowledge of groundwater processes, which significantly limits our ability to assess their importance in the delivery of contaminants to the Reef lagoon. This highlights the need for further investigations, not only in the lower Burdekin and the Johnstone, but more generally across the study areas (and the wider GBR region).

5.4. Implications for Paddock-to-Reef monitoring program

An integrated monitoring, modelling and reporting program has been established to measure and evaluate progress towards the Reef Plan's goals and targets. Catchment-scale water quality monitoring and modelling are important components of this overall Paddock-to-Reef (P2R) program, which encompasses monitoring of a suite of attributes at scales ranging from the farm paddock to receiving waters of the Reef lagoon. The aims of its catchment-scale component, which links paddock-scale and marine monitoring components, are to quantify changes in water quality and contaminant loads at sub-catchment and end-of-catchment scales, and identify potential source areas of contaminants (The State of Queensland 2009b). It is not feasible to monitor contaminant loads discharged by all waterways in the study areas to the Reef lagoon: rather, information from monitoring at selected key sites will be used both to quantify fluxes at those sites and also to test and improve water quality models that can be applied more generally to estimate fluxes, including for those river systems that are not monitored. Eight P2R end-of-catchment stream monitoring sites and one sub-catchment site are located in the three areas that are within the scope of this review (Figs. 1.1–1.3, Table 5.2).

Areas of groundwater discharge

Many streams in the Pioneer Valley receive groundwater discharge along much of their length; e.g., Finch Hatton Creek, Bakers Creek, Sandy Creek and Alligator Creek; they many also include sections of groundwater recharge, or seasonally, both recharge and discharge (Murphy et al. 2005; Howe et al. 2006).

In the lower Burdekin, groundwater discharge to 62 km of the Burdekin River downstream of the Clare Weir was estimated to be 248 ML/d at the end of the 2011 wet season (Cook et al. 2011). This discharge would be represented in samples taken at the P2R end-of-catchment monitoring site on the Burdekin River, for all but the 15 km of river downstream of the Inkerman Bridge (Table 5.2), although as noted in Section 2, the discharge rate varies both seasonally and along this river length. Sampling at this P2R site would include the peak groundwater discharge zone at around 30 km from the river mouth (Cook et al. 2011). By contrast, the P2R site on Barratta Creek is 51.3 km from the mouth (Table 5.2) so sampling there would likely represent only a small proportion (<10%) of the estimated 56 ML/d of groundwater discharged to the 60 km of stream length from the mouth, noting that around 50% of the total groundwater discharge occurs well downstream, in the tidal section of the creek (Cook et al. 2011). At best, monitoring at this P2R site would likely capture on a small portion (1.7 km) of the peak discharge identified between approx. 43 and 53 km from the river mouth (Cook

et al. 2011). An estimated groundwater discharge of 138 ML/d occurs to a 52 km length of the lower Houghton River (Cook et al. 2011), on which there are no P2R monitoring sites.

In the lower Herbert, a mean annual baseflow discharge of 213,200 ML/y was estimated from the alluvium of the intermediate aquifer (S1 and S2 combined, Fig. 2.3) to the Herbert River between 30.1 km and 71.8 km from the river mouth (for a dry year pumping scenario); with a further discharge of 14,444 ML/y between 71.8 and 112 km from the mouth (upstream of the main cane-growing areas) (DSITIA 2012d). These groundwater discharges would be reflected in samples taken at the end-of-system site on the Herbert River (Table 5.2) and they represent approx. 50% of the estimated total groundwater discharge to rivers, streams and drains in the lower Herbert. Approx. 40% of the remaining groundwater discharge occurs to creeks and drains from the S2 and S3 aquifers, while the other 60% is mainly discharge from the S4 aquifer to non-specified rivers, creeks and drains (DSITIA 2012d). Relatively large inputs of groundwater discharge are considered to occur between 14 and 48 km from the mouth of the Herbert River, based on comparisons of nitrate and oxygen isotope ($\delta^{18}\text{O}$) concentrations (Dixon–Jain 2005, cited by DSITIA 2012d).

Table 5.2. The Paddock to Reef program’s end-of-catchment stream monitoring sites in the Wet Tropics, lower Burdekin and Mackay–Whitsunday areas

Region	Sampling site location ¹	Distance upstream from river mouth ² (km)	Areas of groundwater discharge ³ (km from river mouth)	Other significant streams not monitored ⁴
Wet Tropics	Barron R., Myola	27.1		Mulgrave–Russell R.
	N. Johnstone R., Tung Oil	28.5	0–38 km ⁵	Moresby R.
	S. Johnstone R. upstream of Central Mill	18.5 ⁶		Liverpool Ck.
	Tully R., Euramo	17.5	0–30 km ⁵	Murray R.
	Herbert R., Ingham	30.5	14–48 km ⁷ 30.1–71.8 km ⁸	
Burdekin Dry Tropics	Barratta Ck., Northcote	51.3	0–60 km ⁹	Houghton R.
	Burdekin R., Inkerman Bridge ¹⁰	15.0	0–62 km ⁹	
Mackay–Whitsunday	Pioneer R., Dumbleton Weir	16.6	In both cases shallow GW discharge occurs along much of each stream length ^{11,12}	Bakers Ck. Alligator Ck.
	Sandy Ck., Homebush	32.7		

¹From Turner et al. (2011); ²From the Qld Government’s HYDSTRA database; ³In some cases there may be further substantial GW discharge to the main river or to other waterways in the catchment; ⁴Streams also identified as receiving GW discharge; ⁵EHA (2006); ⁶Distance upstream from confluence with the N. Johnstone R. at Innisfail (sub-catchment site); ⁷Dixon–Jain (2005), cited by DSITIA (2009); ⁸DSITIA (2009); ⁹Cook et al. (2011); ¹⁰Note that this sampling site is 25 km downstream of the flow monitoring site at the Clare gauging station; ¹¹Murphy et al. (2005); ¹²Howe et al. (2006)

The lower reaches of the (North) Johnstone River from the river mouth to 38 km upstream are considered to receive permanent drainage from the aquifer (EHA 2006) but only one-quarter of this groundwater flux would be reflected in samples taken at the end-of-system site, 28.5 km upstream from the mouth (assuming groundwater discharge is uniformly distributed). Furthermore, in the broader Johnstone Basin, considerable drainage is thought likely to occur to the Moresby River estuary and to coastal areas between Liverpool and Maria Creeks (DSITIA 2011b), which is consistent with the discharge of fresh groundwater reported offshore in this area (Stieglitz et al. 2010). Other rivers in the Wet Tropics similarly receive considerable groundwater discharge to their

lower reaches. The Tully River for example, has extensive alluvial development on the coastal plain with constant groundwater discharge from the river mouth to 30 km upstream (EHA 2006), just over half of which would not be reflected in samples taken at the end-of-system monitoring site (Table 5.2).

Upstream to downstream increases in nitrate concentrations have been observed in the Herbert and Tully Rivers during low-flow periods and attributed to likely inflows of nitrate-rich groundwater (Furnas 2003). This would be consistent with the large groundwater fluxes to these rivers discussed above. Similar upstream to downstream increases in nitrate concentrations have also been observed in the Mulgrave River (Furnas 2003). In some instances the downstream increases in nitrate concentration were quite marked: e.g., in the Tully River, the median nitrate concentration increased from around 0.03 mg nitrate-N/L upstream to approx. 0.13 mg nitrate-N/L downstream. If indeed these increases in nitrate concentrations are linked to groundwater inflows, it would suggest that; i) nitrate concentrations in groundwater in these areas are considerably higher than upstream concentrations in the respective rivers; and ii) attenuation processes are not adequate to deplete nitrate from groundwater before it enters the streams.

Constructed drains across the study areas vary in depth from around 1 m in the lower Herbert (DSITIA 2012d) up to a maximum of 3 m in the Tully–Murray (DSITIA 2011c). The rapid groundwater discharge rates characteristic of these drains potentially may be important from a water quality perspective, since contaminants in the soil profile may be rapidly entrained and discharged to the surface drainage network, without sufficient residence time in the soil for attenuation to occur (discussed in Sections 4.1–4.3). Evaluating the magnitude of this shallow groundwater flux and the extent to which it would be represented in samples taken at each P2R end-of-catchment monitoring site would require a more detailed assessment than is possible in this review. Nevertheless, it is evident that no monitoring occurs in some areas of significant shallow drainage, including several of those noted above.

Implications for monitoring groundwater fluxes to the Reef lagoon

The present P2R load monitoring program design does not include monitoring of groundwater discharged from aquifers directly to the coast. This omission is likely to be most significant for contaminant fluxes from the Pioneer and the lower Burdekin and much less important (in terms of overall fluxes) in the Wet Tropics, e.g., in the lower Johnstone (Tables 2.1, 5.1). Note that some contaminants possibly may reach marine receiving waters via groundwater pathways and be included in samples taken at the P2R marine water quality monitoring program's inshore sites; however it would not be possible to identify whether these contaminants were derived from groundwater or surface water sources.

It is also clear from Table 5.2 that for river systems where information is available on likely areas of groundwater discharge, sampling at the end-of-system monitoring sites would not capture all of the groundwater fluxes of contaminants. In the Wet Tropics, P2R monitoring at end-of-system sites on Herbert, Tully and Johnstone Rivers would substantially under-represent groundwater discharges and any associated contaminant fluxes (e.g., by up to 50% for the Herbert River site), which potentially is a significant omission, given that discharge to streams is the main route of groundwater fluxes to the Reef lagoon in these systems. Note also that in the Johnstone there are considerable areas of cane downstream of the end-of-system (and sub-catchment) sites, so these sites are not ideal for monitoring cane-related contaminant fluxes in either surface water or groundwater discharges, particularly when areas of cane are the dominant source of the nitrate flux from this river system to the Reef lagoon (Hunter and Walton 2008). Clearly, locating monitoring sites close to river mouths would help overcome these deficiencies. However, many factors require consideration in selecting sites, including the safety and logistics of sampling during major flood events, the confounding effects of tidal flows and the need for reliable quantification of discharge.

While monitoring of river contaminant loads during major runoff events is a crucial component of the assessment of annual fluxes to the Reef lagoon, sampling at these times is less critical for monitoring

of contaminants sourced from groundwater. Given the expected lags in the groundwater response, key times for monitoring of groundwater inflows of contaminants are likely to be those periods from the recession of the hydrograph through to baseflow conditions. Thus, to identify groundwater inflows of contaminants it would be useful to conduct periodic monitoring of stream contaminant levels under these moderate-to-low flow conditions at as many sites as possible, in middle and lower reaches of these river systems. Valuable data and insights into system behaviour can be gained from this approach, even though it does not permit direct quantification of groundwater fluxes, nor confirmation that groundwater is the sole source of any contaminants detected.

It is likely the patterns of groundwater response may differ between river systems, but repeated stream monitoring during between-event periods over several seasons would provide a sound basis for designing a monitoring program tailored to capturing groundwater inflows in each system. The information gained can be used to help determine the extent to which groundwater processes need to be described in catchment models of each system, and can also help improve model conceptualisation and performance. In the Johnstone, for example, where the nitrate flux is predominantly a groundwater-driven process with a slower response time, the use of nitrate data from all monitored sites (including those not sampled during events) was found to greatly enhance model calibration (Walton and Hunter 2009). In certain situations, tracer studies may be warranted; e.g., as carried out in the lower Burdekin by Cook et al. (2004, 2011). While these may be more resource-intensive, they have the potential to provide quite detailed and quantitative information on fluxes of groundwater (and any associated contaminants) in specific riverine and coastal areas.

The overall objective of the P2R integrated monitoring, modelling and reporting program is to measure and report on progress towards the Reef Plan's goals and targets (The State of Queensland 2009b). A key aim of the program is to determine changes in water quality (loads) entering the Reef lagoon as a result of improvements to land management practices. The inevitable lag times between implementing on-farm changes and detecting a response at the end of a large catchment can be very considerable, particularly where groundwater processes that may take decades are involved (Meals et al. 2010). While monitoring at smaller scales (e.g., end of paddock or small sub-catchment) may provide an interim indication of likely changes in surface water fluxes of contaminants from a target area, sampling at such sites may not provide any indication of changes in the groundwater flux, if groundwater from this area is discharged further downstream. It is important to consider groundwater processes and system lags in the monitoring program design and to communicate their implications to stakeholders (Meals 2010).

5.5 Summary of key points

- Widespread areas of groundwater discharge have been mapped along the coastline and in estuaries of the Wet Tropics and the lower Burdekin, highlighting the potential risks to the critical ecosystems in these areas from exposure to any nutrients and herbicides in the groundwater discharged; similar mapping has not been carried out in the Mackay–Whitsunday area
- Temporal patterns of groundwater discharge to the coast following wet season rainfall differ markedly from those of surface waters; the slower response of groundwater discharge is likely to extend the potential exposure period of coastal ecosystems in receiving waters well into the dry season, possibly to all year round
- Exposure of these coastal ecosystems to any contaminants contained in the groundwater may be exacerbated by receiving water circulation patterns in the dry season, which may result in shallow near-shore waters being trapped by the formation of a coastal boundary zone, which restricts the extent of mixing and dilution with other coastal waters
- Across the Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas, little information is available on specific riverine and wetland areas or ecosystems that receive groundwater

discharge (or the volumes discharged), except for rivers and streams in the lower Burdekin: however, middle and lower sections of rivers in the Wet Tropics have been broadly identified as receiving groundwater discharge, while shallow groundwater discharge has been documented to streams and drains in both the Mackay–Whitsunday and Wet Tropics areas

- Fluxes of N, P and PSII herbicides to receiving environments have not been quantified at the point of actual discharge in any of the study areas, whether directly to the coast, or to riverine environments; nor have any studies been conducted of contaminant attenuation in aquifers or interface zones
- Thus, while significant groundwater fluxes may occur (either directly to the Reef lagoon or indirectly via rivers), assessment of the importance of these fluxes for ecosystem health in receiving waters is currently limited by the lack of information on the extent to which contaminants are present in the groundwater discharged
- The P2R monitoring, modelling and reporting program has nine sampling sites across the study areas; the available information suggests that samples taken at these sites generally do not adequately account for groundwater inflows (and any associated contaminants) to respective river systems
- Hence enhancements to the P2R monitoring and modelling programs may be required, including possible investigation of appropriate spatial coverage and sampling times (e.g., moderate to low stream-flow conditions) needed to capture any groundwater inflows of contaminants (if present).

6. Conclusions

The review has provided a brief overview of current knowledge of aquifers and groundwater– surface water connectivity across the Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas, including best-available estimates of groundwater fluxes, and investigations of groundwater discharge directly to the coast and to rivers. Information has been presented on the reported presence of N, P and PSII herbicides in groundwater, and the processes (both natural and anthropogenic) involved in their transport, transformation and attenuation in the root zone and in deeper subsurface environments, including the links to on-farm management.

It is clear from the information presented that there are very many gaps and uncertainties in our present knowledge. The evidence available suggests the possibility that significant fluxes of groundwater may occur, but the extent to which contaminants are present in the groundwater discharged (either directly to the Reef lagoon, or indirectly via rivers) remains unknown. Thus, given the degree of current uncertainties, it is not yet possible to determine with confidence the importance of groundwater flows of N, P and PSII herbicides to the Reef lagoon, relative to surface water flows. However, it is evident that these contaminants are present in groundwater in at least some parts of the Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas, and that groundwater discharge to rivers, streams and directly to the coast occurs widely in all three areas. Moreover, much of the groundwater discharge may occur to sensitive and ecologically important ecosystems, with exposure of coastal ecosystems potentially exacerbated by circulation patterns in the Reef lagoon during drier months of the year.

Key knowledge gaps are summarised in Table 6.1, grouped into four inter-related topics. The issues identified in Table 6.1 are not listed in any order of priority, nor are they rated in terms of their tractability (noting that there may be significant challenges in addressing some of these gaps). Some are specific to a particular area (e.g., anion exchange properties of soils in the Wet Tropics) but most apply across all three study areas, although sometimes to differing extents. For example, current evidence suggests groundwater discharge to rivers and streams in the Wet Tropics is the dominant pathway for groundwater flows to the Reef lagoon in that area, while in the lower Burdekin and Mackay–Whitsunday areas, almost as much groundwater discharges directly to the coast, as to rivers and streams. As noted above however, the extent to which N, P and PSII herbicides are contained in the groundwater discharged remains unknown, in all three areas.

It should be acknowledged however, that there is a considerable body of valuable information now available, including from several recent studies that have significantly advanced our understanding of various aspects of these topics. For example, several studies conducted over the last decade have significantly increased our knowledge of the extent of groundwater discharge to riverine and coastal environments. Furthermore, recent information indicates that in some parts of the lower Burdekin aquifer near the coast, the potential for nitrate attenuation is high (and nitrate concentrations correspondingly low) which suggests the possibility that nitrate levels in groundwater discharged from these areas may be relatively small. However, much more information is needed to establish with confidence whether or not this is the case; further research now in progress will add to the current knowledge base on this topic.

A staged approach is envisaged to address key knowledge gaps, which would include periodic re-evaluation of the key issues and gaps as new information becomes available. This would allow reappraisal of the relative importance of groundwater flows of these contaminants to the Reef lagoon and the need to augment current monitoring and mitigation strategies. It would also help direct further research investments.

Table 6.1. Key knowledge gaps concerning groundwater fluxes of N, P and PSII herbicides to the Reef lagoon in the Wet Tropics, lower Burdekin, and Mackay–Whitsunday areas

Topic	Key knowledge gaps
1. N, P and PSII herbicides in groundwater flows to the Reef lagoon	<ul style="list-style-type: none"> • Volumes of groundwater discharged directly to the coast, to rivers/streams and to drains <ul style="list-style-type: none"> - annually and on a seasonal or monthly basis¹ - pathways / residence times of groundwater discharge, including the occurrence of preferential pathways (bypass flow) • Concentrations of the various forms of N, P and PSII herbicides in groundwater at (or as close as possible to) points of discharge¹ <ul style="list-style-type: none"> - to coasts, rivers and drains - periodically throughout the year • Age of groundwater discharged and likely source/s of contaminants (if present)
2. Receiving environments of groundwater discharge	<ul style="list-style-type: none"> • Identification of specific coastal and riverine locations where groundwater is discharged¹ • The presence of critical ecosystems in receiving environments, and: <ul style="list-style-type: none"> - the extent of their dependency on groundwater - the ecosystem services they provide - threats to their functions/ values from contaminants in groundwater - their potential to mitigate contaminant loads and the need for their conservation or rehabilitation
3. Contaminant transport, transformation and attenuation processes	<ul style="list-style-type: none"> • Understanding and quantification of key processes affecting the fate of contaminants in subsurface environments and the implications for loads discharged via groundwater flows, including <ul style="list-style-type: none"> - spatial/temporal dynamics of key geochemical constituents and processes in aquifers (e.g., nitrate, herbicides, Eh, DOC, Fe²⁺, S²⁻) - the distribution of soils in the Wet Tropics with anion exchange capacity at depth and the loads of nitrate currently held at depth in cane-growing areas - sorption characteristics of PSII herbicides on cane-growing soils - effects of fluctuating or rising groundwater levels on contaminant loads in groundwater discharges, and options for mitigation • The potential for improved on-farm management of nutrients and herbicides to reduce deep drainage losses, while maintaining crop yields
4. P2R monitoring program	<ul style="list-style-type: none"> • In each monitored catchment, identification of locations and seasonal patterns of groundwater discharge, and levels of contaminants in the groundwater discharged (as in 1 and 2 above) • Additional monitoring (sites, sampling times/frequencies) needed to ensure contaminant fluxes via groundwater pathways are adequately represented in flux estimates from monitored catchments to the Reef lagoon • Additional modelling capability needed in conjunction with the above

¹A pre-requisite for addressing knowledge gaps concerning the P2R monitoring and modelling programs

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Appendix 1: Aquifer Descriptions

Table A1.1. Summary of key features of aquifers in the Wet Tropics

Groundwater area	Description
Daintree River	<ul style="list-style-type: none"> There is some alluvial development in the lower reach of the river. Groundwater discharge provides continuous baseflow to the river¹.
Mossman River	<ul style="list-style-type: none"> A shallow, low storage aquifer that receives high recharge. Groundwater discharges continuously to the river²; area under cane decreasing due to urban encroachment¹.
Lower Barron River (0–19 km AMTD)	<ul style="list-style-type: none"> Alluvial delta deposits (clay, sand, gravel) on the coastal plain have little capacity for storage. Urban development is encroaching on cane-growing areas. This section of the river receives groundwater inflows and is perennial (and mostly tidal)^{1,2}.
Lower Mulgrave & Russell Rivers (0–32 km AMTD) Area approx. 325 km ²	<ul style="list-style-type: none"> The area has extensive alluvial development for sugarcane production, with minimal irrigation¹. Cairns City Council has a significant allocation for town water supply. The alluvial sequence is composed of silty/sandy sediments². The alluvium has an average thickness of 45 m. The aquifers consist of poorly sorted sand and gravel, with the main aquifers located 15–45 m below the ground surface. Fractured bedrock and basalt aquifers also occur. The potentiometric surface varies from the ground surface to approx. 13 m depth. Draft water balance estimates indicate discharge to drains is the main pathway of groundwater discharge (approx. 92,000–98,000 ML/y depending on irrigation extractions), compared with total annual discharge to rivers of 1,700–5,100 ML/y³.
Lower Johnstone River (0–38 km AMTD) (including Moresby R., Liverpool Ck. & Maria Cks.) Area approx. 1,755 km ²	<ul style="list-style-type: none"> This is a major cane-producing area with high rainfall. Little water is used for cane irrigation but expansion of banana industry has increased irrigation demand. Surface water and groundwater are closely linked^{1,2}. There are significant thicknesses of alluvium (max. thickness >80 m) and basalt (of variable thickness, max. >90 m). The texture of the alluvium is heterogeneous and includes heavy clays, coarse sand and gravels but much of it is clayey, clay-bound sands or gravel. Most of the alluvium appears to behave as a single unconfined unit. Large and rapid responses of groundwater levels to rainfall occur in some bores, followed by rapid recession, indicating close aquifer–stream connections. Artificial drainage networks occur in some areas to reduce waterlogging of cane. Draft water balance estimates indicate the total annual groundwater discharge to rivers, streams and drains is 289,616 ML/y, and to the coast, 2,726 ML/y⁴.
Lower Tully River (0–30 km AMTD) & Murray River Area approx. 1,470 km ²	<ul style="list-style-type: none"> A high rainfall area; major crops are sugarcane and bananas (grown with negligible irrigation). An extensive artificial network of drains lowers shallow groundwater levels to reduce waterlogging. Rivers and streams are groundwater-fed and perennial¹. The alluvium ranges in thickness (max. >60 m) and comprises varying proportions of clay, silt, sand and gravel, much of it clayey. Most of the alluvium appears to respond as a single unit and shows marked seasonality. A deeper semi-confined aquifer unit occurs in some areas. Recharge of the alluvium occurs directly via rainfall percolation through soils and through transient stream recharge during high stream flows. Groundwater discharge occurs as baseflow to rivers and streams, as discharge to the drainage network (e.g., in the Murray–Riversdale area), as seepage to coastal wetlands and as through-flow to the coast⁵.

Groundwater area	Description
<p>Lower Herbert River (0–80 km AMTD)</p> <p>Area approx. 1,530 km²</p>	<ul style="list-style-type: none"> • Extensive alluvial plains; a major sugarcane production area, with some parts artificially drained to lower watertables; irrigation use is not extensive but groundwater is used for some urban water supplies; groundwater and surface water systems are closely connected^{1,2}. Management issues include saltwater intrusion, acid sulfate soils, declining watertables near wetlands, and pollution from chemical leaching near recharge areas². • The alluvial stratigraphy of the Herbert River delta comprises 4 aquifers at different depths and of differing water quality, with three aquifers predominantly confined and the fourth (uppermost) unconfined. The uppermost aquifer is recharged directly from rainfall, with groundwater levels fluctuating seasonally between approx. 1.5 m and 3.1 m depth. The most extensive and thickest sand unit within the alluvium has an average depth of 25 m; at least one of two mud units in the alluvium is of marine origin. Overall, the natural surface drainage of streams traversing the alluvium is to act as groundwater drains except during transient periods of high stream flow when they act to locally recharge groundwater, which is subsequently and rapidly drained back to the river⁶.

¹EHA (2006); ²KCB (2009); ³DSITIA (2011a); ⁴DSITIA (2011b); ⁵DSITIA (2011c); ⁶Cox (1979) cited by DSITIA (2012d); ⁷DSITIA (2012d).

Table A1.2. Summary of key features of aquifers in the lower Burdekin and Don areas

Groundwater area	Description
<p>Lower Burdekin River (including Burdekin Delta, Haughton River and Barratta Creeks)</p> <p>Area approx. 2,500 km²</p>	<ul style="list-style-type: none"> • The Burdekin R. Delta (0–32 km AMTD) has relatively large groundwater reserves in sandy deltaic sediments that are extensively used for irrigation of sugarcane, other crops and town supply. There is close connection between the aquifer and the river: aquifers are artificially recharged with river water and recharge also occurs from the river. Management issues include rising watertables and saltwater intrusion^{1,2}. • The Burdekin R. (32–56 km AMTD) comprises an extensive alluvial deposit, similar to the Burdekin delta but with more clay. There is close connection between surface water and groundwater near the river. The underlying aquifer is recharged via excess surface water and excess groundwater. Management issues include shallow and rising watertables in some areas of both right and left bank, and groundwater salinity^{1,2}. • The Haughton R. area is a major irrigated cane-growing area. Groundwater recharge occurs via weirs on the river, rainfall and irrigation tail water. Groundwater and surface water are considered closely connected¹. • The Barratta Cks. area is a major irrigated cane-growing area, underlain by sediments deposited by a former channel of the Burdekin River. The creek system is not deeply incised and is mostly confined to the clays of the surficial sequence of the alluvium. Irrigation water does penetrate through to the aquifer but is considered of little consequence for stream–aquifer connections. There is some evidence of limited connection of creek/s to underlying groundwater in the lower reaches¹. • The lower Burdekin floodplain comprises alluvial and deltaic sediments that include layers of gravel, silt, sand and mud. Individual layers are inter-connected and behave hydraulically as one aquifer unit, typically with cleaner fresher water near the surface and more saline water at depth. Fractured granitic basement formations can contribute significantly to groundwater flow and quality. The uppermost (most productive) aquifer is unconfined in some parts of the region and semi-confined in others due to the presence of a surficial clay layer. Recharge from rainfall and leaching from irrigation application comprise the majority of inflow to the aquifer. Groundwater levels show rising trends in the confined alluvial aquifer, while water levels in the unconfined aquifer in the Delta show a long-term fluctuating trend with significant seasonal variation. Large rainfall events can increase groundwater levels up to 5 m in unconfined bores in the Delta and approx. 1 m in confined bores in the semi-confined aquifer. Extensive areas of predominantly estuarine wetlands occur along the coast of Bowling Green Bay³. • Radon tracer studies indicate annual groundwater discharge to Bowling Green Bay is 31,000-170,000 ML/y⁴, while annual groundwater discharge to rivers was estimated to be 14,600 ML/y in 2004 and 161,000 ML/y in 2011 (note, these discharges to rivers are high-end estimates extrapolated from daily measurements at the end of respective wet seasons)^{4,5}. In contrast, draft water balance estimates indicate an average groundwater discharge to the coast (Bowling Green Bay and the Coral Sea)(1981-2006) of 12,231 ML/y³, with previously estimated groundwater discharge to the Coral Sea alone of 1,500-9,000 ML/y⁶.
<p>Don River</p>	<ul style="list-style-type: none"> • Alluvial aquifer with groundwater used for town supply (Bowen) and irrigation (mainly horticulture). The river is ephemeral but closely linked to the aquifer system and is an important source of recharge^{1,2}. The groundwater system acts as a single unconfined aquifer and comprises both unconsolidated alluvial sediments and the underlying weathered granite. Around 85% of recharge occurs via rainfall and irrigation drainage. Water balance estimates based on data for 1989-1997 suggest average annual groundwater discharge to the coast is approx. 2,125 ML/y, around 2-3 times that discharged to the river (which is about one-seventh of groundwater recharge from the river)⁷.

¹EHA (2006); ²KCB (2009); ³McMahon et al. (2012); ⁴Cook et al. (2011); ⁵Cook et al. (2004); ⁶McMahon et al. (2002) cited by McMahon et al. (2012); ⁷Welsh (2002).

Table A1.3. Summary of key features of aquifers in the Mackay-Whitsunday area

Groundwater area	Description
<p>Proserpine River (including Gregory R., Myrtle Ck. & O'Connell R.)</p>	<ul style="list-style-type: none"> • Aquifers are comprised of tertiary sediments and shallow river bed sands which are recharged by releases from Peter Faust Dam to the Proserpine River. The Gregory R. and Myrtle Ck. are perennial, groundwater-fed streams. The O'Connell R. is similar to the Proserpine R. (but with less agricultural development); water is extracted from bed sands but without surface water supplementation^{1,2}.
<p>Pioneer River (including Sandy Ck., Bakers Ck., Alligator Ck., Cattle Ck., Carmilla Ck., Rocky Dam Ck., Cherry Tree Ck., Plane Ck.)</p> <p>Area approx. 2,400 km²</p>	<ul style="list-style-type: none"> • There is a relatively continuous alluvium between the Pioneer R., Sandy Ck., Bakers Ck. and Sandringham Ck. and their groundwater systems are interconnected, while the alluvium of Alligator Ck. is much less connected. Groundwater discharges to all 5 streams and is sourced from volcanic rocks in headwater areas and downstream from the alluvium. Groundwater–surface water relationships are complex due to the complexity of the alluvium (unconsolidated sediments comprising inter-bedded sequences of silts, clays, sandy clays, clayey sands, sands and gravels³), compounded by stream supplementation. The Cattle Ck. area has a shallow alluvium mostly comprised of cobbles and boulders close to the creek, with supplementation provided to some reaches allowing groundwater to be intercepted. The Carmilla Ck. area has only limited groundwater resources; the creek is typically perennial, fed by groundwater from volcanic rocks in upstream reaches and from the shallow alluvium downstream. Rocky Dam Ck. and Cherry Tree Ck. (Koumala) are mostly perennial and fed by groundwater discharge from volcanic rocks; groundwater is used for town supplies² and there is some irrigation use. Plane Ck. is perennial and groundwater-fed, with only a limited groundwater resource¹. • The Pioneer Valley groundwater system is comprised mainly of an unconfined alluvial aquifer (of variable depth up to approx. 40 m) with underlying and adjacent weathered and fractured rock aquifers, all of which react similarly to recharge and discharge events. Responses to rainfall are rapid. Some streams act as groundwater drains during periods of flow (e.g., Alligator Creek, Bakers Creek) and drains have been constructed in certain areas to reduce groundwater levels. Groundwater is used for irrigation, domestic, industrial and urban supplies. Generally, groundwater discharges to streams when the stream levels are below groundwater levels: draft water balance estimates indicate average discharges (1991-2003) of 10,256, 915 and 4,067 ML/y to the Pioneer R., Bakers Ck., and Sandy Ck., respectively. Additional discharge to coastal margins and estuarine areas of major streams is estimated to be an average (1991-2003) of 15,523 ML/y⁴.

¹EHA (2006); ²KCB (2009); ³Reid et al. (2009); ⁴Murphy et al. (2005).

Appendix 2:

Principles of Nutrient and Herbicide Management of Cane for Minimising Groundwater Contamination⁶

Nutrient management

Some principles of nutrient management for cane crops, which may help minimise the risk of groundwater contamination by nutrients, are outlined in Table A2.1. The interpretation and application of these principles will vary from farm to farm, however the key message is to provide the optimum amount of nutrients at the right time.

Table A2.1. Summary of key principles of nutrient management of cane crops that may help minimise risks of groundwater contamination

Principle	Details	Gaps or barriers to implementation of improved practices
Nutrient inputs: additional sources considered All sources of nutrients are accounted for in meeting crops full nutritional requirements	Calculation of nutrient application rates to consider nutrient and amelioration needs of soil; e.g., for sodic soils, this would include application of gypsum	Perceived lack of calibration in existing nutrient calculators to fit all cane growing situations
	Mill mud/ash application	Availability of spreaders to distribute mill mud/ash evenly across cane blocks
	Legumes	Some issues about how much N is available to the plant crop if a rain event occurs after beans have been incorporated or sprayed out
Application timing for plant (optimal growth stages) Improve timing to allow optimal crop uptake of applied nutrients	Timing of nutrient applications to be in-line with crop requirements	Difficult to achieve as it may require removal of irrigation infrastructure to allow fertilisation after first irrigation or rain
	Split application of fertiliser	There is a risk that growers will not be able to apply a second round of fertiliser if heavy rains fall during the growing season – if this happens, growers are required to apply fertiliser aerially at a much higher cost and with no yield benefit

⁶ Information provided by the Reef Water Quality Unit, Department of Environment and Heritage Protection (unpublished)

Principle	Details	Gaps or barriers to implementation of improved practices
	<p>Use of nitrification inhibitors, urease inhibitors or slow release fertilisers</p> <p>Some forms of fertiliser can reduce off-site losses, whether through leaching or volatilisation</p>	<p>Cost, requires further research to establish economic benefits</p>
<p>Application timing: consideration of weather</p>	<p>Ensure loss of applied product is minimised through educated forecast assessment</p>	<p>High level of weather variability across cane growing areas of Queensland</p>
<p>Accuracy of nutrient delivery to minimise off site losses</p> <p>Identify appropriate application method for soil type and site conditions, e.g. surface, sub-surface, fertigation, etc.</p>	<p>Apply nutrients in locations readily available for crop uptake to minimise offsite losses, e.g.:</p> <ul style="list-style-type: none"> • surface broadcast increases offsite losses and reduces quantity of available nutrient for plant uptake • subsurface beside stool is generally readily available for uptake 	<p>Availability of machinery</p>

Herbicide management

Some principles of herbicide management of cane crops, which may help minimise the risk of groundwater contamination by herbicides, are outlined in Table A2.2.

Table A2.2. Summary of key principles of herbicide management of cane crops that may help minimise risks of groundwater contamination

Principle	Details	Gaps or barriers to implementation of improved practices
<p>Use optimal rates of herbicides</p> <p>Using only the optimal rate of herbicide will minimise the amount of herbicide available to contaminate groundwater</p>	<p>Calculation of optimal herbicide rates should consider:</p> <ul style="list-style-type: none"> • label conditions • regular calibration and use of correct nozzles and pressure • weed species and growth stage • weed pressure within blocks • farm and block characteristics, e.g., <ul style="list-style-type: none"> - soil type - crop stage and variety - areas of erosion - drainage - slope <p>Using multiple methods of control can reduce herbicide application rates – e.g.,:</p> <ul style="list-style-type: none"> • knock downs and pre-emergents • biological • fallow or rotation crops • green cane trash blanketing (GCTB) • mechanical control • hygiene control 	<p>There may be issues with the use of fallow crops or GCTB in some areas</p> <p>Use of mechanical control may lead to increased risk of soil erosion</p>
<p>Timing of herbicide application</p> <p>Herbicide applications should be timed to maximise uptake by weeds and minimise the risk of groundwater contamination.</p>	<p>The timing of herbicide applications should consider:</p> <ul style="list-style-type: none"> • rain forecasts and other weather risk factors • seasonal conditions, e.g., start of monsoon cycle • irrigation schedule 	

Appendix 3: Glossary⁷

Term	Definition
Abiotic	Relating to the non-living components of an environment or system (see biota).
Adsorption	Adherence of ions or molecules to the surface of solids.
Adsorption complex	Collection of various organic and inorganic substances in soil and sediments that are capable of adsorbing ions and molecules.
Aerobic	(i) Having molecular oxygen as a part of the environment; (ii) growing only in the presence of molecular oxygen, such as aerobic organisms; (iii) occurring only in the presence of molecular oxygen.
Alluvium	A general term for clay, silt, sand, gravel or similar unconsolidated material deposited during comparatively recent geologic time by a stream or other body of running water.
Aluminium oxyhydroxide (AlHO₂)	Aluminium oxyhydroxide is found as one of two well defined crystalline phases, which are also known as the minerals boehmite and diaspore.
Ammonium (NH₄⁺)	A cation comprised of one nitrogen atom and four hydrogen atoms, from which ammonia gas can be formed under alkaline conditions.
AMTD	Adopted middle thread distance. Distance in kilometres from the mouth of a watercourse.
Anaerobic	(i) The absence of molecular oxygen. (ii) Growing in the absence of molecular oxygen (such as anaerobic bacteria). (iii) Occurring in the absence of molecular oxygen (as a biochemical process).
Anammox	Microbial reaction in which ammonium is oxidised by nitrite to dinitrogen gas under anaerobic conditions.
Anion	An atom or group of atoms that is negatively charged because of a gain in electrons. Electrons are negatively charged elementary particles.
Anion exchange capacity	The total ionic charge of the adsorption complex active in the adsorption of anions.
Anoxic	Without free oxygen or combined forms of oxygen (e.g., as found in NO ₃ ⁻)
Anthropogenic	Caused or produced by human activities.
Aquifer	A permeable rock formation, group of formations, or part of a formation that stores and transmits sufficient groundwater to yield significant quantities of water to wells, bores and springs.
Artificial recharge	The deliberate replenishment of the groundwater by means of spreading basins, recharge wells, irrigation, or other means to induce infiltration of surface water.
Attenuation	Reduction in value or amount.
Bacteria	Any of a group of microscopic single-celled organisms that live in enormous numbers in almost every environment on the surface of Earth.

⁷ Principal sources of information:

ANZECC & ARMCANZ (2000)

Britannica Online Encyclopedia: www.britannica.com

British Geological Survey: www.bgs.ac.uk/research/groundwater/resources/glossary.html

Cox, ME, Groundwater Systems NQB614, unpub. class notes, Queensland University of Technology

McMahon et al. (2011)

Soil Science Society of America: www.soils.org/publications/soils-glossary#

Sugar Industry Glossary: www.acfa.com.au

US Geological Survey: www.or.water.usgs.gov/projs_dir/willgw/glossary.html

Term	Definition
Bank Storage	The storage of water in an aquifer adjacent to and interconnecting with a surface water body so that a change in a stage of the adjacent surface water body causes a change in storage of water in the aquifer.
Basalt	A fine-grained, basic igneous rock composed largely of pyroxene and calcium-rich plagioclase in about equal amounts.
Baseflow	Natural discharge of groundwater from an aquifer, via springs and seepages, to rivers.
Bedrock/basement	A general term for the rock, usually solid, that underlies soil or other unconsolidated material.
Benthic	Organisms living in or on the sediments of aquatic habitats, or processes relating to these organisms.
Bioavailable	Readily taken up and transformed by microorganisms or readily taken up by plants. Also referred to as labile.
Biodiversity	The variety of life forms, including the plants, animals and microorganisms, the genes they contain and the ecosystems and ecological processes of which they are a part.
Biota	All living organisms present in a particular environment.
Block target yield approach	See Target yield approach
Bypass flow	The process whereby free water and its constituents move by preferred pathways through a porous medium. Also called preferential flow.
Catchment	The area of land drained by a river and all of its tributaries.
Cation	A positively charged ion.
Cation exchange	The interchange between a cation in solution and another cation in the boundary layer between the solution and surface of negatively charged material such as clay or organic matter.
Clay	A naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when dried or fired.
Composting	A controlled biological process which converts organic constituents, usually wastes, into humus-like material suitable for use as a soil amendment or organic fertilizer.
Compound (chemical compound)	Any substance composed of identical molecules consisting of atoms of two or more chemical elements.
Confined aquifer	A confined aquifer is a completely saturated permeable formation of which the upper and lower boundaries are impervious layers.
Contaminant	An undesirable substance not normally present or an unusually high concentration of a naturally occurring substance in water or soil.
Deep drainage	The drainage of soil water downward by gravity below the maximum effective depth of the root zone toward storage in subsurface strata.
Decomposition	Microbial breakdown of organic matter.
Degradation	The process whereby a compound is transformed into simpler compounds.
Denitrification	Reduction of nitrogen oxides (usually nitrate and nitrite) to molecular nitrogen or nitrogen oxides with a lower oxidation state of nitrogen by bacterial activity (denitrification) or by chemical reactions involving nitrite (chemodenitrification). Nitrogen oxides are used by bacteria as terminal electron acceptors in place of oxygen in anaerobic respiratory metabolism.
Dinitrogen gas (N₂)	Molecular nitrogen gas.
Discharge	The volume of water that passes a given location within a given period of time.

Term	Definition
DT₅₀	The time taken for dissipation of 50% of the applied mass of a pesticide. Loss could be due to degradation or physical movement from the point of interest.
DNRA	Dissimilatory nitrate reduction to ammonium. Anaerobic microbial process in which nitrate is reduced to nitrite and then to ammonium.
DSITIA	Department of Science, Information Technology, Innovation and the Arts
Dunder	Liquid waste that results from the fermentation of molasses in the production of ethanol.
Ecology	The study of organisms and how they interact with each other and their physical surroundings.
Ecosystem	A dynamic combination of plant, animal and micro-organism species and communities and their non-living environment and the ecological processes between them interacting as a functional unit.
Eh	A measure of oxidation-reduction potential, expressed in units of millivolts (mV). A high (positive) Eh indicates an oxidising environment; a low (negative) Eh indicates a reducing environment.
Electrical conductivity (EC)	Measure of the ability of material to conduct an electrical current. For water samples, it depends on the concentration and type of ionic constituents in the water and temperature of the water.
Enzyme	Any of numerous proteins that are produced in the cells of living organisms and function as catalysts in the chemical processes of those organisms.
Estuary	A seaward end or the widened funnel-shaped tidal mouth of a river valley where fresh water comes into contact with seawater and where tidal effects are evident; e.g., a tidal river, or a partially enclosed coastal body of water where the tide meets the current of a stream.
Exchangeable anion	A negatively charged ion held on or near the surface of a solid particle by a positive surface charge and which may be easily replaced by other negatively charged ions.
Exsolution	The process of separating or precipitating from a solid crystalline phase.
Ferric iron (Fe₃⁺)	An oxidised form of iron.
Ferrous iron (Fe₂⁺)	A reduced form of iron.
Fertilizer	Any organic or inorganic material of natural or synthetic origin (other than liming materials) that is added to a soil to supply one or more plant nutrients essential to the growth of plant.
Filter mud (mill mud)	The insoluble matter extracted from cane juice during the clarification process after the mud is filtered and washed to recover the sugar it contains. The solids consist of mainly field soil, fibre, calcium phosphate, denatured protein and a small amount of sugar.
Filterable reactive phosphorus	Forms of phosphorus in solution that pass through a 0.45 µm filter and react positively in the chemical test for orthophosphate without prior digestion. May include other simple inorganic phosphates as well as orthophosphate (PO ₄ ³⁻).
Flow path	The subsurface course a water molecule or solute would follow in a given groundwater velocity field.
Floodplain	The nearly level land that borders a stream and is subject to inundation under flood-stage conditions unless protected artificially. It is usually a constructional landform built of sediment deposited during overflow and lateral migration of the stream.
Flux	The time rate of discharge of groundwater (and/or its constituents) per unit area of a porous medium measured at right angles to the direction of flow.

Term	Definition
Fractured rock	A general term for rock which has been deformed to contain cracks, joints, faults, and other breaks by earth movement to form voids. The voids may contain water.
Freshwater	Water that contains less than 1,000 milligrams per litre (mg/L) of dissolved solids.
Gaining stream	A stream or reach of a stream which receives inflow of groundwater.
Geochemical	Relating to the chemical composition of the earth's crust and the chemical changes that occur there.
Groundwater	That part of the subsurface water that is in the saturated zone.
Groundwater-dependent ecosystems	Those ecosystems that derive some or all of their water requirements from groundwater.
Groundwater discharge	Flow of water from the zone of saturation.
Groundwater gradient	The change in static or total head per unit of distance in a given direction. The direction is that which yields a maximum rate of decrease in head.
Groundwater system	A groundwater reservoir and its contained water. Also, the collective hydrodynamic and geochemical processes at work in the reservoir.
Habitat	The native environment or kind of place where a given animal or plant naturally lives or grows.
Half-life	The time taken for the concentration of a pesticide to be reduced by half under controlled laboratory conditions.
Herbicide	An agent, usually chemical, for killing or inhibiting the growth of unwanted plants.
Heterogeneity	A characteristic of a medium in which material properties vary from point to point.
Heterogeneous	Non-uniform in structure or composition throughout.
Homogeneity	Pertaining to a substance having identical characteristics everywhere.
Hydraulic conductivity	The rate at which water can move through a porous medium.
Hydraulic gradient	Slope of the watertable or potentiometric surface. The change in static head per unit of distance in a given direction. If not specified, the direction generally is understood to be that of the maximum rate of decrease in head.
Hydraulic head	The height above a datum plane (such as sea level) of the column of water that can be supported by the hydraulic pressure at a given point in a groundwater system. For a well, the hydraulic head is equal to the distance between the water level in the well and the datum plane.
Hydrogeology	The study of the distribution and movement of groundwater in the soil and rocks of the Earth's crust (commonly in aquifers).
Hydrolysis	The chemical reaction which occurs between a substance and water.
Hyporheic zone	The transition zone over which the fluctuations in exchange between surface water and groundwater occur.
Igneous rock	Rock formed from the cooling and solidification of magma, and that has not been changed appreciably by weathering since its formation.
Immobilization	The conversion of an element from the inorganic to the organic form in microbial or plant tissues.
Impermeable layer	A layer of solid material, such as rock or clay, which does not allow water to pass through.
Infiltration	The movement of a fluid into a solid substance through pores or cracks; in particular, the movement of water into soil or porous rock.
Infiltration	The downward entry of water into the soil or rock.

Term	Definition
Inorganic nitrogen	Forms of nitrogen not combined with carbon; commonly found as nitrate, nitrite and ammonium.
Inorganic phosphorus	Forms of phosphorus not combined with carbon; commonly found as orthophosphate (PO_4^{3-}) and polyphosphates (chains of orthophosphate).
Interface	A point or zone where interaction occurs between two systems.
Interflow	Water that infiltrates into the soil and moves laterally through the upper soil horizons until intercepted by a stream channel.
Ion	A charged atom or group of atoms that has gained or lost one or more electrons. An electron is a negatively charged elementary particle.
Isotope	One of two or more forms of atoms of a chemical element with nearly identical chemical behaviour but with different atomic masses and physical properties.
K_d	Pesticide sorption coefficient. The ratio of the sorbed-phase concentration of a pesticide to the solution-phase concentration at equilibrium, expressed in units of mL/g. It is a measure of how tightly the pesticide binds to soil particles; the greater the K_d value, the less likely a chemical will leach.
K_{oc}	Sorption coefficient (K_d) per unit of soil organic carbon; expressed in units of mL/g.
Labile	Readily taken up and transformed by microorganisms or readily available to plants. Also referred to as bioavailable.
Leaching	The process by which soluble materials in soil, such as salts, nutrients, pesticides or other contaminants, are washed into a lower layer of soil or are dissolved and carried away by water.
Legume	A member of the Leguminosae family of plants which often have a symbiotic relationship with a bacterium (Rhizobium) that fixes nitrogen in the plants' roots. Also refers to the pods or seeds of such a plant. Symbiosis in this case is the association between organisms of two different species in which each is benefited.
Losing stream	A stream or reach of a stream in which water flows from the stream bed into the ground.
Lysimeter	A device for measuring percolation and leaching losses from a column of soil under controlled conditions.
Macroalgae	Multi-cellular marine algae.
Megalitre (ML)	One million litres (1,000 cubic metres).
Microsite	A small volume of soil or sediment where biological or chemical processes differ from those of the soil/sediment as a whole, such as an anaerobic microsite of a soil aggregate or the surface of decaying organic residues.
Mill mud	The insoluble matter extracted from cane juice during the clarification process after the mud is filtered and washed to recover the sugar it contains. The solids consist of mainly field soil, fibre, calcium phosphate, denatured protein and a small amount of sugar.
Mineralization	The conversion of an element from an organic form to an inorganic form as a result of microbial activity.
Mineralogy	A scientific discipline concerned with all aspects of minerals, including their physical properties, chemical composition, internal crystal structure, and occurrence and distribution in nature and their origins in terms of the physicochemical conditions of formation.
Mitigation	Reduction in severity or intensity.
Model	A conceptual, mathematical, or physical system obeying certain specified conditions, whose behaviour is used to understand the physical system to which it is analogous in some way.

Term	Definition
Nitrification	Biological oxidation of ammonium to nitrite and nitrate.
Nitrogen fixation	A natural (or industrial) process by which atmospheric dinitrogen gas (N ₂) is converted to ammonium (NH ₄ ⁺).
Nitrous oxide (N₂O)	A colorless gas that (amongst other things) is an atmospheric pollutant.
Nitrate (NO₃⁻)	An anionic, oxidised form of nitrogen that contains three oxygen atoms.
Nitrite (NO₂⁻)	An anionic, oxidised form of nitrogen that contains two oxygen atoms.
Order of magnitude	Differing from a value by a factor of ten.
Organic carbon (organic compound)	Any of a large class of chemical compounds, often derived from living organisms, in which one or more atoms of carbon are bonded to atoms of other elements, most commonly hydrogen, oxygen, and/or nitrogen. A few carbon-containing compounds such as carbonate and cyanide are classified as inorganic carbon, not organic carbon.
Organic matter	Plant and animal residues, or substances made by living organisms; all are based upon carbon compounds.
Organic nitrogen	Organic compound that contains nitrogen.
Organic phosphorus	Organic compound that contains phosphorus.
Organisms	Living things such as plants, animals and bacteria.
Oxic	Oxygenated or aerobic.
Oxidation	The loss of one or more electrons by an ion or molecule. Electrons are negatively charged elementary particles.
Oxidised nitrogen	Inorganic nitrogen comprising nitrate and nitrite ions.
Paleochannels (palaeochannels)	Old or ancient watercourses that are inferred from the geology.
Perched groundwater (perched watertable)	Unconfined groundwater separated from an underlying body of ground water by an unsaturated zone. Its watertable is a perched watertable. Perched groundwater is held up by a perching bed whose permeability is so low that water percolating downward through it is not able to bring water in the underlying unsaturated zone above atmospheric pressure.
Percolation	The downward movement of water through the unsaturated zone.
Permeability	The capacity of a porous material for transmitting a fluid.
Pesticide	Any toxic substance used to kill animals or plants that cause economic damage to crop or ornamental plants or are hazardous to the health of domestic animals or humans. All pesticides interfere with normal metabolic processes in the pest organism and often are classified according to the type of organism they are intended to control; e.g., herbicide, insecticide, fungicide.
pH	The measure of acidity or alkalinity of a solution, numerically equal to 7 in neutral solutions.
Photosynthesis	The process by which plants, algae and certain bacteria transform light energy into chemical energy.
Photosystem II	The protein complex that absorbs light as the first stage of photosynthesis.
Piezometer	A device used to measure groundwater pressure head at a point in the subsurface.
Pollution	Specific impairment of water quality by agricultural, domestic, or industrial wastes to a degree that has an adverse effect upon any beneficial use of water, including ecosystem protection.
Potentiometric surface	An imaginary surface representing the elevation and pressure head of groundwater and defined by the level to which water rises in a well or piezometer. The water table is a particular potentiometric surface of an unconfined aquifer.

Term	Definition
Preferential flow	The process whereby free water and its constituents move by preferred pathways through a porous medium. Also called bypass flow.
PSII herbicide	Herbicides that impair a plant's photosynthetic activity by disrupting its Photosystem II processes.
Radon	A colourless, odourless, tasteless, radioactive and almost completely un-reactive gas that is relatively rare in nature because all of its isotopes are short-lived and because its source, radium, is scarce. Trace levels of radon occur in soils, sediments and groundwater but it rapidly dissipates into the atmosphere on exposure to the earth's surface. ^{222}Rn can be used as an environmental tracer to estimate and locate groundwater baseflow into streams, differentiate between native groundwater and bank return flow, and allow mixing processes within the near-stream environment to be assessed.
Radium	A highly radioactive metallic element which is the parent radionuclide to radon gas and alpha rays. In the ^{238}U decay series ^{226}Ra (half-life of 1622 years) decays to ^{222}Rn (half-life of 3.825 days).
Recharge	The quantity of water that is added to a groundwater reservoir from areally distributed sources such as the direct infiltration of rainfall or leakage from an adjacent formation or from a watercourse crossing the aquifer.
Redox potential	The oxidising or reducing capacity of a solution relative to a reference potential.
Redox reaction	A chemical reaction in which an atom or molecule loses electrons to another atom or molecule. Also called oxidation-reduction reaction. Oxidation is the loss of electrons; reduction is the gain in electrons. Electrons are negatively charged elementary particles.
Reduction	The gain of one or more electrons by an ion or molecule. Electrons are negatively charged elementary particles.
Respiratory process	Process by which organisms produce energy.
Riparian	Abutting a watercourse, wetland or lake or through which a watercourse flows or a lake is situated.
Riparian zone	Pertaining to banks of a river, wetland or lake (usually more broadly defined as the strip of land tens of metres wide along the banks of the stream).
Riverine	Associated with rivers and streams.
Salinity	The amount of soluble salts in a water or soil.
Saturated zone	The zone of an aquifer where the voids in the rock or soil are completely filled with water at a pressure greater than atmospheric. The water table is the top of the saturated zone in an unconfined aquifer.
Seawater intrusion	The entry of seawater into a coastal aquifer. It may be caused by over pumping fresh water from the aquifer or insufficient natural head on the fresh water aquifer. Seawater is denser than fresh water and it may form a wedge beneath the fresh water adjacent to the coast.
Sediment	Particles at the bottom of the water column of rivers and the sea generally derived from soil on land. In the plural, the word refers to all kinds of deposits by water, wind and ice. They may be consolidated or unconsolidated.
Seepage	The slow movement of water through small cracks, pores or interstices of a material into or out of a body of surface or subsurface water.
Slightly disturbed ecosystem	Ecosystems in which aquatic biological diversity may have been adversely affected to a relatively small but measurable degree by human activity. The biological communities remain in a healthy condition and ecosystem integrity is largely retained. (As defined by ANZECC & ARMCANZ 2000.)

Term	Definition
Sorption	The removal of an ion or molecule from solution by adsorption or absorption. The term is often used when the exact nature of the mechanism of removal is not known.
Spring	A discrete place where groundwater flows naturally from a rock, soil or sediment onto the land surface or into a body of surface water.
Stratigraphy	Concerning the origins, composition, distribution and succession of geological strata. Strata are sheet-like masses of sedimentary rock or earth of one kind lying between beds of other kinds.
Sub-catchment	The area of land drained by a tributary of a river.
Submarine groundwater discharge (SGD)	The direct discharge of groundwater from onshore coastal aquifer systems via seabed sediments into the near-shore marine environment. Also includes seawater flow into and out of sediments such as caused by wave and tide-induced flow oscillations and seasonal inflow and outflow of seawater into the aquifer.
Symbiosis	An association between organisms of two different species, often in which each is benefited.
Target yield approach	For the cane industry in Queensland, a method of determining the amount of nitrogen fertiliser to apply to a crop in a specific farm block. The approach is based on setting a realistic block target yield for the coming season and then using the industry benchmark recommendation of 1.4 kg applied N/t cane for first 100 t/ha and then 1 kg applied N/t cane thereafter to calculate the amount of N required for that yield. The yield target takes into account: (i) past block performance over three cane cycles; and (ii) the expected growing conditions in the coming season (e.g., using a seasonal forecasting tool). The applied N required for the target yield is then reduced by the amounts of N contributed from the following sources: legume crop residues, irrigation water, mineralisation of soil organic matter, inputs of mill by-products and other organic amendments, and pre-existing mineral N in the soil profile. This approach aims at improving the efficiency of N fertiliser use on cane.
Tertiary	The geologic time period from 65 to 2 million years ago.
Transport	Conveyance of solutes and particulates in flow systems.
Trash blanket	Layer of sugarcane crop residues retained on the soil surface after harvest.
Trigger value	The concentration of a water quality constituent (indicator) below which there is a low risk that adverse ecological effects will occur. Follow-up investigation is recommended if a trigger value is exceeded.
Unconfined aquifer	An aquifer where there are no impermeable barriers (confining layers) between the water table and the surface. The upper boundary of the saturated zone, the water table, is at atmospheric pressure.
Unconsolidated sediments	Soil or sediments, which have not been altered, cemented or compacted since their deposition.
Unsaturated zone	The zone between the land surface and the water table. The pore spaces are partly filled with air and contain water at less than atmospheric pressure. Also known as the vadose zone.
Upconing	Process by which saline water underlying freshwater in an aquifer rises upward into the freshwater zone as a result of pumping water from the freshwater zone

Term	Definition
Water balance	A procedure whereby water inputs and outputs are accounted for in a given aquifer leaving a balance called the storage. The main tasks include: identifying the components contributing to the natural recharge and discharge of the aquifer; analysing the human impacts on the aquifer in terms of abstraction, artificial recharge, seepage from irrigation channels and leaching from irrigation application; quantifying interactions between the surface water bodies and the aquifer; and estimating historical gains or losses of groundwater and comparing these to the storage change estimated from the observed historical groundwater levels. The general equation for the water balance is: Change in Storage = Inflow – outflow.
Water cycle	The circuit of water movement from the oceans to the atmosphere and to the earth and its return to the atmosphere through various stages or processes such as precipitation, interception, runoff, infiltration, percolation, storage, evaporation, and transportation.
Waterlogging	Saturation or near saturation of the soil with water.
Water quality	The chemical, physical, and biological characteristics of water, usually in respect to its suitability for a particular purpose.
Water resource plan	A plan approved under the relevant sections of the Queensland Water Act 2000.
Watertable	A surface which defines the top of the saturated zone in an unconfined aquifer at which the pressure of the water is equal to that of the atmosphere.
Weathering	The breakdown and changes in rocks and sediments at or near the Earth's surface produced by biological, chemical and physical agents or combinations of these.
Wetland	Land that has a predominance of hydric soils and is inundated or saturated by surface water or groundwater at a frequency and duration sufficient to support a prevalence of vegetation typically adapted for life in saturated soil conditions. A hydric soil is one that formed under conditions of saturation, flooding, or ponding long enough to develop anaerobic conditions in the upper part.
Wonky hole	Location where groundwater discharge occurs from confined submarine aquifers that are associated with buried paleochannels of riverine or estuarine origins.
Zooxanthellae	Flagellate protozoa (or algae) which live in other protozoa and in some invertebrates (e.g., corals). A protozoan is an organism, generally single-celled, that uses organic carbon as a source of energy. Flagella are hair-like structures capable of whip-like lashing movements that enable locomotion.