Proceedings of the 13th International Marine Biological Workshop

The Marine Fauna and Flora of Moreton Bay, Queensland

Volume 54, Part 1

Editors: Peter J.F. Davie & Julie A. Phillips

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PO Box 3300, South Brisbane 4101, Australia
Phone 06 7 3840 7555
Fax 06 7 3846 1226
Email qmlib@qm.qld.gov.au
Website www.qm.qld.gov.au

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Relationships between groundwater composition and stimulation of the cyanobacterium *Lyngbya majuscula*

Kathleen S. AHERN

University of Queensland, Water Studies, Environmental Engineering, Brisbane, Qld 4072, Australia. Email: kattyahern@gmail.com

Shane M. POINTON
Colin R. AHERN

Queensland Department of Natural Resources and Water, Indooroopilly, Brisbane, Qld 4068, Australia.

James W. UDY

University of Queensland, Water Studies, Environmental Engineering, Brisbane, Qld 4072, Australia; South-east Queensland Water Corporation, 240 Margaret St, Brisbane, Qld, 4002, Australia.

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ABSTRACT

The Pumicestone Passage/Deception Bay region of southeast Queensland, Australia, has experienced increased frequency and severity of blooms of the toxic benthic cyanobacterium *Lyngbya majuscula*. It is hypothesised that blooms are the result of landuse changes in the surrounding catchments leading to increased nutrient and organic matter loads to waterways. Previous studies investigating the response of *L. majuscula* to diluted groundwaters from across Deception Bay/Pumicestone Passage showed groundwater from acid sulfate soils, exotic pine plantations and *Melaleuca* vegetation significantly stimulated *L. majuscula* photosynthetic response in laboratory bioassays. The results of the previous study are expanded by investigating the composition of these 74 groundwaters to ascertain what factors contribute to the observed differences in *L. majuscula* response. A multiple regression analysis showed the total iron, pH, conductivity, total phosphorus and dissolved organic carbon contents in groundwater accounted for 58% of the variation in *L. majuscula* response. Total iron content of the groundwater had the highest correlation accounting for 28% of the variation in response. Other significant correlations included ammonium nitrogen, total phosphorus and electrical conductivity. Significant responses to iron, phosphorus and nitrogen concentrations in experiments involving addition of pure chemicals has previously been found for both laboratory based bioassays and *in situ* field experiments. The response to electrical conductivity is probably the result of a correlation with acid sulfate soils whose groundwater has been shown to significantly stimulate *L. majuscula* response. As landholders commonly identify and manage land through vegetation, soils, geology and landuse, these categories were used to statistically assess groundwaters. Based on the groundwater relationships, land with *Melaleuca*, pine or *Casuarina* vegetation, or with Hydrosols, Podosols or acid sulfate soils present, or formed from marine sediments, needs to be carefully managed to limit nutrient export that could boost *L. majuscula* growth Our conclusions can be used to confirm or adjust hazard ratings in the Nutrient Hazard Model. ❑ *cyanobacteria, groundwater, growth, landuse, Lyngbya majuscula, Moreton Bay, nutrients.*

Harmful algal blooms are becoming more numerous, widespread and persistent in nutrient-enriched tropical and subtropical marine ecosystems (Paerl 1988). One species of concern is the benthic filamentous, non-heterocystous nitrogen-fixing cyanobacterium *Lyngbya majuscula* which in recent years, has bloomed in eutrophic estuaries, embayments and reef environments across the world (Diaz *et al.* 1990; Albert *et al.* 2005). Blooms have had adverse environmental and economic impacts, including directly overgrowing and smothering intertidal and subtidal benthic communities such as seagrass and coral (Stielow & Ballantine 2003). Additionally, *L. majuscula* contains secondary metabolites and toxins (reviewed in Osborne *et al.* (2001)), which have caused asthma, dermatitis and eye irritation in humans, and have been linked with increased tumour occurrence in marine turtles (Arthur *et al.* 2006).

Increased frequency and severity of freshwater and marine blooms of *Lyngbya* species in several different systems worldwide (Diaz *et al.* 1990; Speziale & Dyck 1992; Dennison *et al.* 1999), has been linked to anthropogenic nutrients, supplied through terrestrial runoff and groundwater. Similarly, blooms of *L. majuscula* in northern Deception Bay, southeast Queensland, Australia, have been linked to landuse changes resulting in increased loads of nutrients and dissolved organic matter in the creeks and water-bodies adjacent to the bloom site, especially after significant rainfall events (Ahern *et al.* 2007b; Dennison *et al.* 1999; Albert *et al.* 2005). In an effort to reduce the intensity and severity of blooms, local and state regulatory authorities expressed a desire to identify areas and landuse activities most likely to supply/transport bioavailable nutrients and organic matter to bloom sites to allow management to focus on the higher-hazard areas. However, the amount and form of nutrients/organic matter in runoff, or transported in groundwaters from a particular parcel of land, is influenced by complex interactions involving geology, soils, vegetation, present and past landuse, and human activities (Pointon *et al.* 2004). While nutrient analyses of the soils and groundwater from different areas within the catchment are important, biological information on *L. majuscula* growth is necessary to effectively interpret such data.

Laboratory-based biological assays have been employed to test *L. majuscula* growth responses to soils, leachates and groundwaters from different areas across the Pumicestone Passage/Deception Bay catchments (Ahern *et al.* 2003, 2006a; Albert *et al.* 2005). Preliminary bioassays showed that the addition of diluted soil extracts (Albert *et al.* 2005) and groundwaters (Ahern *et al.* 2003) from exotic pine plantations and *Melaleuca* communities on acid sulfate soils (ASS) stimulated *L. majuscula* productivity. Using this information, combined with Geographic Information System (GIS) coverages, published information, and limited laboratory analyses of soils and groundwaters, the first version of a 'Nutrient Hazard Model' (termed 'Hazard Model' for the remainder of the paper) was developed to predict areas vulnerable to the export of nutrients (Pointon *et al.* 2004). Since then, the model has gone through an iterative process of revisions as new data or findings become available with map outputs from the revisions of the earlier Hazard Model being used to support *Algal Blooms* policy 2.4.7 within the *Southeast Queensland Regional Coastal Management Plan* (EPA 2006). To further improve the Hazard Model, a more comprehensive bioassay study of 74 groundwaters representing 10 major landuse/vegetation/soil systems from across the Deception Bay/Pumicestone Passage catchments was conducted. This showed groundwater from areas of ASS, exotic pine plantations and *Melaleuca* vegetation (paperbark swamps) significantly stimulated *L. majuscula* photosynthesis (Ahern *et al.* 2006a).

OBJECTIVES

This study expands on the detailed bioassay work of Ahern *et al.* (2006a) by investigating the physico-chemical and nutrient composition of the 74 groundwaters to ascertain the main factors contributing to the observed differences in *L. majuscula* photosynthetic response. Relationships between *L. majuscula* response and groundwater properties/nutrients are explored using a range of statistics, in order to confirm and/or improve predictive ability of the latest version of the Hazard Model (Pointon *et al.* 2008).

As landholders commonly identify and manage land by features such as vegetation, soils, geology and landuse, these themes, with the addition of ASS and geology have been used to statistically assess groundwaters. This will support the identification of areas requiring greater management attention and higher hazard ratings in the Hazard Model.

METHODS

STUDY AREA

Sampling was conducted in the catchments of rivers and steams that flow into Deception Bay and Pumicestone Passage, Southeast Queensland, Australia (Fig. 1). These catchments have been extensively impacted by human development, including rapidly expanding urban and rural/ residential areas adjacent to landuse changes such as: livestock grazing; the removal of natural vegetation; extensive *Pinus elliottii* plantation forestry; horticulture; agriculture; sand/gravel extraction; and, intensive poultry farming. These catchments adjoin the shallow tidal seagrass beds of northern Deception Bay that have been subject to summer blooms of *L. majuscula* (Fig. 1). Bribie Island, where there were numerous sites, is often simply referred to in the text as 'Bribie'.

SITE SELECTION AND SAMPLING

Shallow groundwater was collected from 74 sites representing 10 major landuse/vegetation/ soil combinations (Table 1), chosen because of their large spatial area, close proximity to waterways, or the results from previous laboratory bioassays (Ahern *et al.* 2006a). At each site, piezometers wells (50 mm inside diameter and slotted at the required depth to allow groundwater inflow) were installed using a percussion-assisted drilling device (Geoprobe®, Salina, Kansas, USA) to auger a hole (~60 mm diameter) to a depth that intercepted the shallow (<3 m) water-table or shallow aquifer. In waterlogged areas (such as *Melaleuca* swamps on Bribie I.), the 'surface water' was also collected. Collection of water samples was not undertaken until at least 7 days after the well was installed to allow for settling. Prior to collecting the samples, the wells were purged using a submersible pump to remove 'older water' present and allow inflow of groundwater into the well.

Samples were collected by pumping groundwater directly from the well through an inline filter into clean (acid and deionised water washed) bottles. To minimise oxygen contamination, bottles were overfilled to ensure no air bubbles were present prior to capping. For dissolved nutrient and organic carbon analyses, sampled water was filtered through 0.45 µm membrane filters. Samples for dissolved metal analysis were also filtered and fixed with 5mL of 70% nitric acid (v/v). For ferrous (Fe^{2+}) iron concentrations, a measured aliquot of the 0.45 µm filtered groundwater was immediately added to preweighed ferrozine solution in tubes in the field before any oxidation could occur. Samples high in ferrous iron content (as indicated by intense purple colour) were repeated with a smaller aliquot. All water samples were immediately placed on ice and on return to the laboratory stored at <4^{o} C in the dark until used in the bioassays (within 24 hours) or analysed for nutrients.

At the same time as piezometer installation, an undisturbed soil core (40 mm in diameter) was collected using Geoprobe® hollow barrels. Soil depth increments were sampled depending on the horizonation of the particular soil, but generally were 0–10, 20–30, 50–60, 80–90, 110–120, 140–150, 180–200, 230–250 and 280–300 cm. The soil cores were described according to the Australian Soil and Land Survey Field Handbook (McDonald *et al.* 1990) and classified as per The Australian Soil Classification system (Isbell 1996), Great Soil Group system (Stace *et al.* 1968) and A Factual Key for the Recognition of Australian Soils (Northcote 1984). Acid sulfate soils were identified by soil profile morphology, peroxide field pH tests (Ahern *et al.* 1998) and confirmed by laboratory analyses.

NUTRIENT ANALYSIS

Water samples were analysed for pH (4500H) and electrical conductivity (2510A). Soluble ammonium (NH_4-N) (4500NH3H), oxidised nitrogen (NO_x-N) (4500NO3-I) and orthophosphate (PO_4-P) (4500PG) were determined on a Foss STAR5000, Flow Injection Analysis Colorimeter (APHA/AWWA/WEF, 2005). Dissolved Kjeldahl nitrogen and phosphorus were also determined by Flow Injection Analysis Colorimetry after Kjeldahl digestion. Dissolved inorganic (5310A) and organic carbon (5310D) was determined using a Non-Dispersive Infra Red (NDIR) detection cell (APHA/AWWA/WEF, 2005). Dissolved metal contents were determined

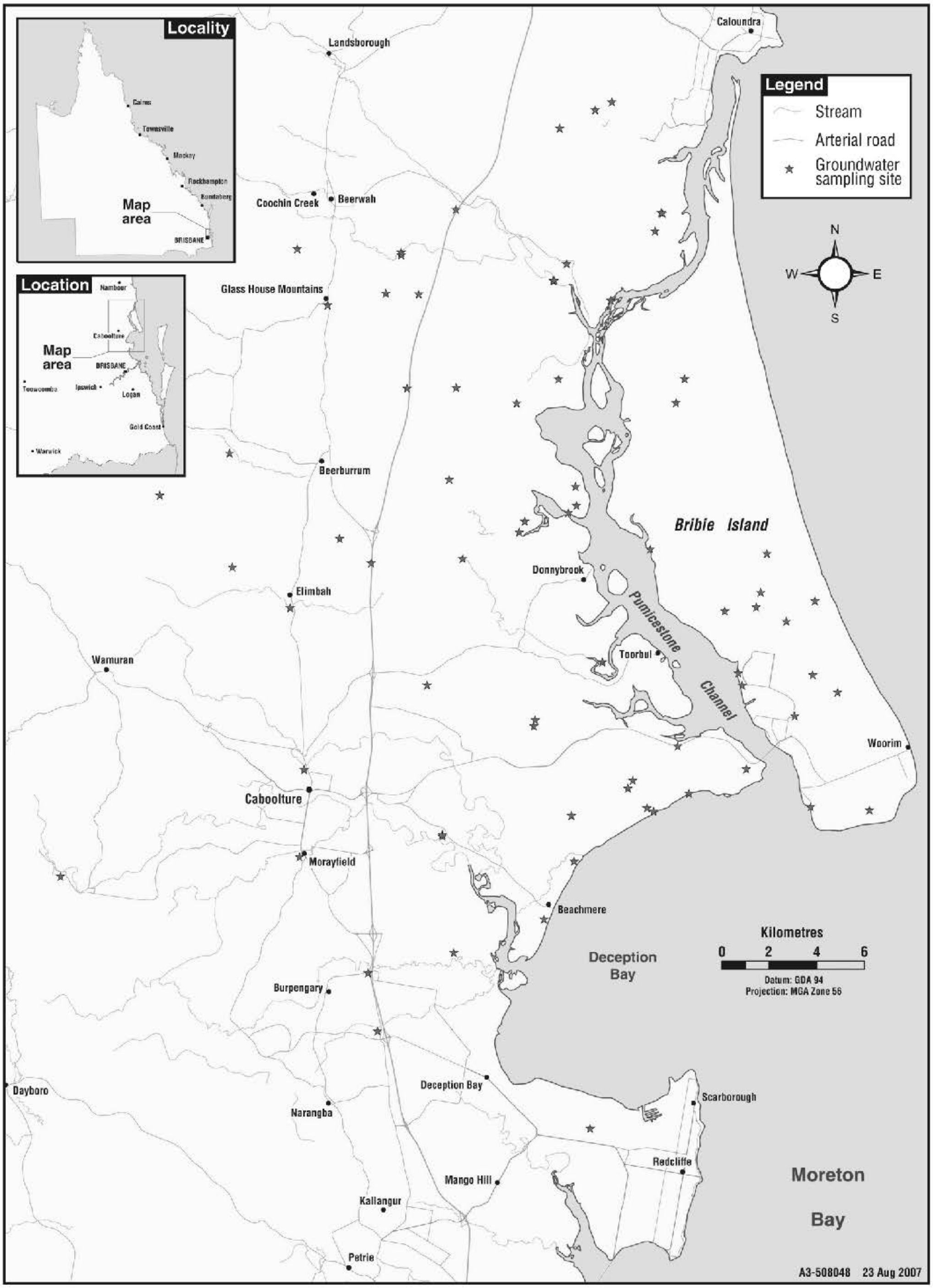

FIG. 1. Map of Deception Bay/Pumicestone Passage catchments showing sampling locations of the 74 shallow groundwater sites.

Table 1. Description of the 10 landuse/vegetation/soil systems used in groundwater experiments of *L. majuscula* bioassays (adapted from Ahern *et al.* 2006b).

Group	ASS presence	Landuse/vegetation class	No. of sites
Melaleuca	ASS	Remnant native vegetation	12
	No	Remnant native vegetation	4
Casuarina	ASS	Remnant native vegetation	9
	No	Remnant native vegetation	6
Disturbed' and/or cleared landscapes	ASS	Urban, canal development, sand extraction, horticulture	10
	No	Urban, horticulture, grazing	6
Pine on mainland	No	Plantation forestry (younger, older and cleared plantations)	9
Pine on Bribie Is			6
Eucalypt	No	Remnant native vegetation	7
Wallum heathland	No	Remnant native vegetation	5

using Inductively Coupled Plasma Optical Emission Spectrometry (ICPOES) (Varian Vista Pro and Thermo TJA IRIS) (APHA/AWWA/WEF, 2005). Ferrous iron concentrations were determined by the Ferrozine method (Stookey 1970) which involved reading the purple colour developed with Ferrozine reagent on a spectrophotometer (absorption peak at 562nm) and calibrating against standard solutions. For laboratory analysis of ASS, a selection of soil depths increments were analysed in the laboratory following the ASS methods of Ahern *et al.* (2004).

TESTING *LYNGBYA* RESPONSE TO GROUNDWATERS

L. majuscula photosynthetic response to each of the 74 groundwaters was ascertained by laboratory based biological assays using a ^{14}C-bicarbonate radioisotope technique documented in Ahern *et al.* (2006a).

DATA SYNTHESIS AND ANALYSIS

The program Statistica™ was used to perform all statistical analysis in the current study. To ensure assumptions of a linear model were met, visual diagnostics of the residuals were undertaken to check that the variances of the dependant variables were homogeneous and followed a normal distribution. If necessary, the variables were transformed by an appropriate power selected with a Boxcox test and the residuals rechecked for normality and variance homogeneity. When appropriate, Fisher's least significant difference (LSD) was used to test for significant differences between means. Data on the nutrient concentrations (total iron, ferrous iron, total phosphorus, phosphate, total nitrogen, ammonium, NOx and DOC) and properties (conductivity and pH) of the groundwaters were correlated with *L. majuscula* response (i) individually and (ii) via multiple regression. Data used for the correlations and multiple regression were taken from all the 74 groundwater sites, except for extreme outliers, which were identified Mahalanobis distances. Additionally, data were organised and analysed according to various groupings including the 10 groups in Table 1, ASS status, vegetation type, general soil classification and broad geology.

MULTIPLE REGRESSION OF *LYNGBYA* RESPONSE VERSUS GROUNDWATER PROPERTIES

A multivariate stepwise regression was used to determine which groundwater properties/nutrients or combination of properties/nutrients best explained variation in *L. majuscula* productivity. Explanatory variables (groundwater properties/nutrients) used in the analysis were total iron, ferrous iron, total phosphorus, phosphate, total nitrogen, ammonium and NOx. Conductivity, pH and dissolved organic carbon (DOC) concentrations were also included as they can affect the chemical state, solubility and presumably influence the bioavailability of nitrogen, phosphorus and iron to *L. majuscula*.

A forward stepwise selection of parameters (total iron, ferrous iron, total phosphorus, phosphate, total nitrogen, ammonium, NOx, DOC, pH and conductivity) was performed using stepwise regression. The starting point was a model with no parameter effects (except intercept). Every possible parameter was included in the model in turn, and its effect was proved with Akaike's information criterion. At each step, the best explanatory (i.e., most informative) variable was selected. During the stepwise process, the effect of the elimination of previously selected parameters and the inclusion of a new one was valued, and the action that most improved the model was performed. This was continued until the most optimal model, comprising the best explanatory variables, was found. Finally, the significance of stepwise-model parameters was tested (using *F* statistics) and non-significant parameters (P > 0.05) were removed.

ANALYSIS OF GROUNDWATER DATA

Data from the different groundwaters were grouped and statistically analysed in five different ways according to: i) the 10 major landuse/soil/vegetation combinations (Table 1); ii) ASS status; iii) dominant vegetation; iv) soil order; and, v) the dominant geology/parent material. The purpose of this was to help isolate the main nutrients/groundwater properties contributing to differences in *L. majuscula* response between groups and secondly, to assist in the identification of areas in the Deception Bay/Pumicestone Passage area with high intrinsic potential to store and/or supply nutrients for *L. majuscula* growth. The later was deemed necessary to support the compilation and validation of the 'Hazard Model' compiled to identify areas vulnerable to supply and/or export of nutrients to *L. majuscula* blooms in southeast Queensland (Pointon *et al.* 2008).

For the 10 major landuse/soil/vegetation systems, a one-way ANOVA was conducted on each different nutrient and groundwater property. Similarly, separate one-way ANOVAs were conducted on vegetation (*Melaleuca*, *Casuarina*, wallum, eucalypt, pine and cleared/disturbed), soil order (Podosols, Hydrosols, Chromosols, Dermosols and Rudosols) and dominant geologies/parent materials (marine, alluvium and continental). Another one-way ANOVA was conducted on three vegetation types (*Melaleuca*, 'disturbed' and *Casuarina*) growing on ASS and non-ASS.

RESULTS AND DISCUSSION

LYNGBYA RESPONSE TO GROUNDWATER

The multiple regression of *L. majuscula* productivity with groundwater properties found that the dependant variables in order of significance were: total iron, pH, conductivity, total phosphorus and dissolved organic carbon (DOC), (the significance level, standardised Beta and B are shown in Table 2). The final model explained 58% of the variation in *L. majuscula* response (R^2= 0.58; $F_{6,60}$=16.1; P <0.0001), and is expressed as:

Y = 0.12 total Fe + 0.76 pH + 0.11 conduct. + 0.16 total P   0.11 DOC + 0.42

These five dependant variables along with a sixth, ammonium, which did not make a significant contribution to improving the R^2 of the regression, are discussed in detail below.

ROLE OF KEY NUTRIENTS

Nitrogen-fixing cyanobacteria, such as *L. majuscula* (Lundgren *et al.* 2003) are not necessarily dependant on an external source of nitrogen and instead phosphorus (essential for growth) and iron (required for photosynthesis and nitrogen fixation) often become limiting (Whitton & Potts 2000). The current study found concentrations of total iron, total phosphorus and ammonium in groundwater were individually significantly correlated with the photosynthetic response of *L. majuscula* in the bioassays (Table 3), as reported in Ahern *et al.* (2006a).

Iron. Iron is an essential micronutrient for the growth of all aquatic organisms and is particularly important for the nitrogen-fixation cyanobacterium such as *L. majuscula,* being an essential component in the nitrogenase enzyme (Paerl *et al.* 1987). Total iron in the groundwater had the highest (r = 0.53) and most significant (P < 0.001) correlation with *L. majuscula* photosynthetic response; with total iron accounting for 28% of the variation (Table 3). This agrees with previous laboratory studies (Gross & Martin 1996; Dennison *et al.* 1999; Ahern *et al.* 2006b), and with *in situ* field studies at two

Table 2. Multiple regression of *L. majuscula* relative productivity response to groundwaters vs various independent variables: $R^2= 0.58$; $F_{6, 60} =16.1$; $P < 0.0001$.

	Beta	**B**	***P* level**
Intercept		0.42	$P = 0.39$
Total iron	0.503	0.12	**$P < 0.0001$**
pH	0.376	0.76	**$P < 0.001$**
Conductivity	0.353	0.11	**$P < 0.001$**
Total phosphorus	0.283	0.16	**$P < 0.01$**
DOC	0.236	0.11	**$P < 0.05$**

locations in Moreton Bay (the Eastern Banks (Ahern *et al.* 2007a) and Deception Bay (Ahern *et al* 2008) — where rapid growth of *L. majuscula* was observed following the addition of organically chelated iron to the water column.

As expected there was a highly significant ($P < 0.001$) correlation (r = 0.61) between ferrous and total iron, but while there was also a highly significant correlation between *L. majuscula* photosynthesis and total iron, the correlation with ferrous iron alone (r = 0.13) was not significant ($P > 0.05$). This is likely due to instability of the ferrous ion when added at a 1:19 ratio to slightly alkaline seawater (pH ~ 8.2), and open to the air for oxidation over the 5 days of the bioassay. The soluble organically complexed iron in groundwaters (included in total iron measurement) was probably the main source for the *L. majuscula* photosynthetic response, especially because it can undergo photoreduction and release short-lived ferrous iron species into solution (Waite & Morel 1984) which *L. majuscula* is known to uptake directly (Rose *et al.* 2005).

Phosphorus. Phosphorus is essential for all metabolic processes and consequently has been commonly recorded as limiting for cyanobacteria growth (Whitton & Potts 2000). Table 3 shows total phosphorus in the groundwater was significantly ($P < 0.05$) correlated with *L. majuscula* photosynthesis (r = 0.28); accounting for 8% of the variation in response. This positive correlation agrees with previous laboratory studies where phosphorus additions have been shown to enhance photosynthesis, growth and nitrogen fixation rates of cultured (Elmetri & Bell 2004) and field collected (Kuffner & Paul 2001; Ahern *et al.* 2007a) *L. majuscula*. In-situ field experiments at two locations in Moreton Bay have also demonstrated stimulation of *L. majuscula* growth from phosphorus additions (Ahern *et al.* 2007a; Ahern *et al.* 2008).

Total phosphorus was strongly (r = 0.65) and significantly ($P < 0.001$) correlated with phosphate concentrations, but phosphate itself did

Table 3. Correlation matrix of relative photosynthetic response of *L. majuscula* to groundwater nutrient concentrations/properties and correlations between those properties. Values in bold are significant at $P < 0.05$.

Property	Relative *Lyngbya* response	pH	Cond.	Total Fe	Ferrous Fe	Total P	Phos p.	Total N	NH_4^+	NOx
pH	0.13									
Conductivity	**0.50**	**0.25**								
Total iron	**0.53**	**0.35**	**0.50**							
Ferrous iron	0.13	0.24	0.07	**0.61**						
Total phosphorus	**0.28**	0.09	0.03	0.11	0.17					
Phosphate	0.00	0.05	0.15	0.02	0.23	**0.65**				
Total nitrogen	0.07	0.05	0.05	0.23	**0.34**	**0.50**	**0.52**			
Ammonium	**0.42**	0.20	**0.47**	**0.55**	**0.38**	0.18	0.12	**0.40**		
NOx	**0.30**	0.00	0.00	**0.41**	**0.28**	0.10	0.09		0.09	
DOC	0.04	0.05	0.00	0.16	0.20	**0.46**	**0.56**	**0.55**	0.14	0.03

not significantly correlate (r = –0.004) with the *L. majuscula* photosynthetic response. This anomaly may be due to either adsorption of phosphate on freshly precipitated iron hydroxy-oxides, or direct reaction of the phosphate with iron to form insoluble iron phosphate (Menon *et al.* 1990; Chiswell *et al.* 1997) under the circum-neutral pH of partially aerated seawater. The total phosphorus would have included organically complexed phosphorus which was probably the available form during the 5 days of the bioassay.

Nitrogen. Nitrogen is an essential macronutrient for growth of marine organisms. There was a highly significant ($P < 0.001$) correlation (r = 0.42) between ammonium and *L. majuscula* photosynthetic response; with ammonium accounting for 18% of the variation. Although *L. majuscula* is capable of high nitrogen fixation rates (Lundgren *et al.* 2003; Elmetri & Bell 2004) and thus not reliant on an inorganic nitrogen supply from the water column or sediments, nitrogen fixation is energetically expensive, and autotrophic cyanobacteria preferentially uptake inorganic nitrogen from the surrounding seawater (Paerl *et al.* 1987). Cyanobacteria prefer to acquire nitrogen in the form of ammonium (Tandeau de Marsca 1993) as assimilation of nitrate or nitrite requires reduction (via nitrate and nitrile reductase enzymes) to ammonium (Oliver 2000). The addition of inorganic nitrogen has been shown to stimulate *L. majuscula* growth under both laboratory and *in situ* field conditions (Ahern *et al.* 2007a; Ahern *et al.* 2008).

There was a significant ($P < 0.05$) negative correlation (r = –0.30) of the oxidised inorganic nitrogen form (NOx) and *L. majuscula* photosynthetic response. This is likely because ammonium ions tend to dominate under reducing conditions (common in groundwaters), while nitrate and nitrite ions are more prevalent under oxidising conditions (more common with surface waters). The current study supports this view because ferrous iron in the groundwaters (the common form of iron under reduced conditions) was positively correlated (r = 0.38; $P < 0.01$) with ammonium, but negatively correlated (r = 0.28; $P < 0.05$) with NOx (Table 3).

Dissolved Organic Carbon. It has been hypothesised that dissolved organic carbon (DOC) acts as a chelator maintaining iron solubility during transport to bloom sites (Albert *et al.* 2005). Rose & Waite (2003) showed that the formation of iron-organic complexes result in considerably higher, and more persistent concentrations of bioavailable iron and phosphorus in the water column. However, in the current study DOC concentration in the groundwater was not shown to be significantly correlated (r = 0.04) with *L. majuscula* response. This suggests that the measurement of the DOC concentrations alone is not useful for predicting *L. majuscula* response, and the situation is much more complex.

O'Sullivan (2003) found a diverse array of natural organic complexers in the soils, groundwaters and waterways of the Deception Bay study area. Organic matter from different areas was shown to have different complexing strengths, with that from pine plantations being a very strong iron chelator (Rose & Waite 2003). The ability of organic material to complex iron and keep it soluble/bioavailable at higher pH (such as seawater at about pH 8) under aerated or partially oxidising conditions, is the main reason for interest in DOC. In this large dataset with a wide range of vegetations and soils, there was no significant relationship between DOC and ferrous or total iron. In contrast to iron, DOC was significantly ($P < 0.01$) correlated with phosphate (r = 0.56), total nitrogen (r = 0.55) and total phosphorus (r = 0.46).

pH. Groundwaters pH was not significantly ($P > 0.05$) correlated (r = 0.13) with *L. majuscula* response. As expected, pH was negatively ($P < 0.01$) correlated (r = 0.34) with total iron. Iron is more mobile and soluble under lower pH (acidic) conditions (Byrne & Kester 1976; Liu & Millero 2002). Additionally, ASS that have been partially oxidised are acidic, and release iron as a by-product of the oxidation of iron sulfide. The pH of a soil and groundwater have been shown to influence the solubility of nutrients, with both iron and phosphorus minerals generally being more soluble under acidic conditions (McKenzie *et al.* 2004). However, a soil or groundwater with a low pH does not necessarily mean high levels of soluble nutrients. On Bribie, for example, the Podosol soils are highly acidic but the groundwaters are relatively low in total iron because there is minimal iron source in the highly leached Pleistocene sands, with iron coatings on the sand grains long since removed (Farmer *et al.* 1983).

Conductivity. Electrical conductivity (an indicator of salinity) of the groundwater had a strong and highly significant correlation (r = 0.50) with *L. majuscula* response. Given that the groundwater solutions were diluted at a 1:19 ratio with filtered seawater in the bioassays, the conductivity of the groundwaters is unlikely to have directly affected photosynthetic response in the bioassay. The strong correlation is probably because groundwaters from ASS areas are known to produce significant *L. majuscula* responses (Ahern *et al.* 2006a), but also have higher conductivity. The low pH and high iron concentrations of the groundwaters from ASS areas are also reflected in the negative correlation (r = 0.25; $P < 0.05$) of conductivity with pH, and the positive correlation with total iron (r = 0.50; $P < 0.001$).

Complexity and interactions. The complexity of the nutrient status in groundwater means that its make-up is likely to be unique for any given parcel of land, and extrapolation over an area of more than 1200 km^2 (Fig. 1) is not useful. However, total iron, total phosphorus and ammonium are important to the *potential* of an area to export nutrients important for *L. majuscula* growth, but this potential may be modified or enhanced by the pH and DOC of the groundwater or soil.

THE TEN LANDUSE/VEGETATION/SOIL GROUPINGS

To discover any common reasons for photosynthetic *L. majuscula* responses, the present study investigated the nutrient composition and properties of groundwaters (Fig. 2) from 10 landuse/vegetation/soil groupings (Table 1) which were tested in *L. majuscula* biological assays in Ahern *et al.* (2006a). Analyses of variance showed significant differences between the '10 groups' for pH, conductivity, ferrous iron, total iron, phosphate, ammonium, NOx and DOC (Table 4; Fig. 2). Ahern *et al.* (2006a) found groundwaters from three groups, i) *Melaleuca* on ASS, ii) 'disturbed' on ASS, and iii) *Casuarina* on ASS, produced the most significant ($P < 0.0001$) *L. majuscula* photosynthetic responses (mean ratios 1.8, 1.8, 2.2 times the control respectively; Fig. 2i). The present study has found these three groups share a low pH (means 4.5 ± 0.44; 4.9 ± 0.47; and 4.9 ± 0.56 respectively; Fig. 2ii); very high total iron (means 107 ± 65; 30 ± 15; 54 ± 30 mg L^{-1} respectively; Fig. 2 v); and very high ferrous iron concentrations (means 42 ± 24; 37 ± 17; 40 ± 19 mg L^{-1} respectively). The means for

Table 4. One-way ANOVA of nutrient concentrations/properties of groundwaters collected from the 10 landuse/vegetation/soil systems, dominant vegetation, soil order and geology groups in the Deception Bay/Bribie Island study area. Values in bold are significant, * $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$; **** $P < 0.0001$; ^{NS} non-significant.

Water property	Units	Ten Landuse/ vegetation/soil systems	Soil orders	Vegetation	Geology
pH		**$F_{9,64}$ = 2.4***	**$F_{4,53}$ = 2.9***	$F_{5,68}$ = 0.9^{NS}	**$F_{2,71}$ = 7.7*****
Conductivity	µS cm 1	**$F_{9,64}$ = 15.6*******	**$F_{4,53}$ = 3.7***	**$F_{5,68}$ = 8.1*******	**$F_{2,71}$ = 14.7*******
Total iron	mg L 1	**$F_{9,64}$ = 4.3******	**$F_{4,53}$ = 3.2***	**$F_{5,68}$ = 2.4**	**$F_{2,71}$ = 11.0*******
Ferrous iron	mg L 1	**$F_{9,64}$ = 3.8******	**$F_{4,44}$ = 7.6*******	$F_{5,58}$ = 1.2^{NS}	**$F_{2,71}$ = 3.9***
Total phosphorus	mg L 1	$F_{9,62}$ = 1.7^{NS}	$F_{4,51}$ = 0.6^{NS}	$F_{5,66}$ = 0.8^{NS}	$F_{2,71}$ = 0.1^{NS}
Phosphate	mg L 1	**$F_{9,64}$ = 2.2***	**$F_{4,53}$ = 3.5***	**$F_{5,68}$ = 2.4***	$F_{2,71}$ = 2.0^{NS}
Total nitrogen	mg L 1	$F_{9,62}$ = 1.5^{NS}	$F_{4,51}$ = 0.4^{NS}	$F_{5,66}$ = 0.4^{NS}	**$F_{2,71}$ = 4.8***
Ammonium	mg L 1	**$F_{9,64}$ = 3.4****	$F_{4,53}$ = 0.1^{NS}	**$F_{5,68}$ = 2.6***	**$F_{2,71}$ = 3.5***
NOx	mg L 1	**$F_{9,64}$ = 2.2***	$F_{4,53}$ = 0.8^{NS}	$F_{5,68}$ = 1.8^{NS}	$F_{2,71}$ = 0.8^{NS}
DOC	mg L 1	**$F_{9,63}$ = 8.5*******	$F_{4,52}$ = 2.4^{NS}	**$F_{5,67}$ = 3.4****	**$F_{2,71}$ = 3.7***

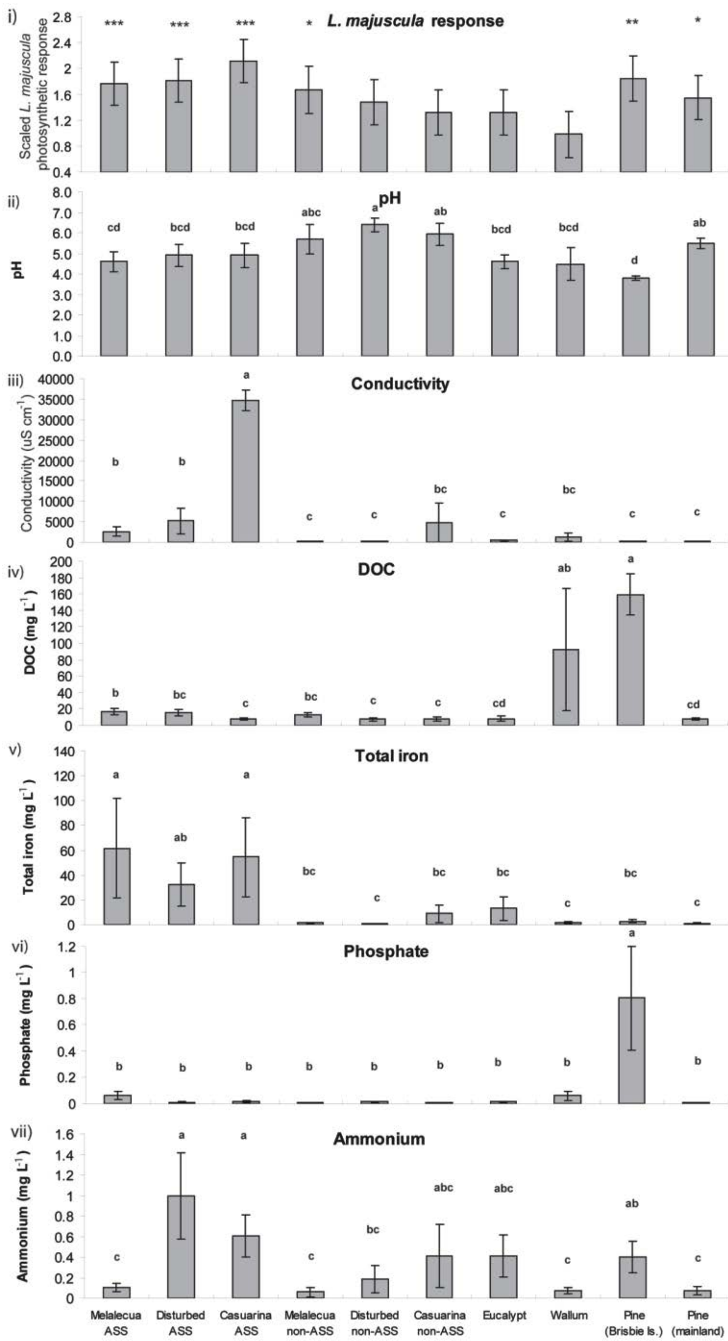

FIG. 2. Mean (±SE) of nutrient concentrations/properties of the groundwaters collected from the '10 landuse/vegetation/soil systems' in the Deception Bay/Bribie Island study area: (i) *L. majuscula* scaled response relative to the control (1.0 = control); (ii) pH; (iii) conductivity; (iv) DOC; (v) total iron; (vi) phosphate; and (vii) ammonium. Level of significant difference of *L majuscula* response compared to the control mean is shown by * $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$. For the remaining graphs (ii to vii) means followed by a common letter are not significantly different at $P > 0.05$.

conductivity on these ASS are also high (2700 ± 1100; 4700 ± 2900; 35000 ± 2500 µS cm^{-1} respectively).

Ahern *et al.* (2006a) also found that groundwaters from '*Melaleuca* non-ASS' ($P < 0.05$), 'pine plantations from Bribie Island' ($P < 0.01$) and 'pine plantations from the mainland' ($P < 0.05$) resulted in significantly higher *L. majuscula* responses than the control by 1.7, 1.9 and 1.6 times respectively (Fig. 2i). Waters from these three groups were characterised by low pH (5.7 ± 0.62; 3.8 ± 0.10; and 5.5 ± 0.25; Fig. 2ii) and very low conductivity (210 ± 64; 310 ± 58; 140 ± 23µS cm^{-1}; Fig. 2 iii). 'Pine from Bribie Island' had relatively high mean total phosphorus (0.55 ± 0.31 mg L^{-1}) and phosphate concentrations (Fig. 2vi), probably as a result of fertiliser application at planting. However, mean total phosphorus concentrations in groundwaters from 'pine on the mainland' (mean 0.046 ± 0.006 mg P L^{-1}) were a tenth of that on Bribie. Bribie commonly has impermeable coffee rock layers resulting in perched watertables (Armstrong & Cox 2002). The '*Melaleuca* non-ASS' also had low phosphorus (mean total P = 0.068 ± 0.044 mg L^{-1}; Fig. 2vi). The total iron concentrations of the above three groups were low (means 1.3 ± 0.43; 2.7 ± 1.3; 1.1 ± 0.55 mg L^{-1}) with virtually all total iron present in the ferrous form.

ACID SULFATE SOILS VERSUS NON-ACID SULFATE SOILS

Acid sulfate soils contain significant amounts of iron sulfides, formed by bacterial reduction in water-logged anaerobic conditions when seawater (or sulfate-rich water) mixes with sediments containing iron and organic matter. Very acidic soil solutions and groundwaters are common in ASS areas because when these soils are exposed to air during drainage or disturbance, they oxidise to produce sulfuric acid and various iron compounds. The term ASS also includes soils that have partially oxidised to produce very acidic soils with pH <4.

The mean pH of groundwater from ASS areas in our study (4.75) was significantly ($P < 0.01$) lower than from non-ASS areas (6.04) (Table 5). We found mean total iron concentrations (67 ± 27 mg L^{-1}) in groundwaters from ASS areas were significantly ($P < 0.0001$) and substantially higher (18 times) than the mean from the non-ASS areas (3.8 ± 2.5 mg L^{-1}). Mean ferrous iron concentration from ASS areas was also 11 times higher than from non-ASS areas, but the difference was not significant ($P > 0.05$). When only ASS groundwater sites are considered, there was a highly significant, strong negative correlation between pH and ferrous iron ($r_{26} = -0.63$) as well as pH and total iron ($r_{26} = -0.61$), showing that higher iron levels were associated with the most acidic groundwaters. The ferrous iron and total iron concentrations of groundwaters from ASS areas were also highly correlated ($r_{26} = 0.87$).

Strongly acidic soils solutions can dissolve insoluble soil minerals, supplying soluble nutrients including phosphorus, nitrogen and trace elements to the soil solution and ultimately the groundwater. Certainly, in the present study mean total phosphorus concentrations were 2.2 times and significantly ($P < 0.05$) higher in groundwaters from ASS areas compared with non-ASS areas (Table 5). Mean phosphate concentrations were also 3.4 times higher in the ASS areas but the difference was not significant due to higher variability. Similarly, the mean total nitrogen and ammonium concentrations were higher (by 1.6 and 2.2 times respectively) in the groundwaters from ASS compared with non-ASS, though the difference was only significant for total nitrogen ($P < 0.05$).

The formation of coastal ASS in a marine environment was reflected in the high salinity (mean EC 12660 ± 2850 µS cm^{-1}) of the ASS groundwater samples. The conductivity of the waters from ASS areas was substantially (6.7 times) and significantly ($P < 0.0001$) higher than the equivalent non-ASS (Table 5).

Ahern *et al.* (2006a) reported groundwaters from ASS areas resulted in significantly higher *L. majuscula* photosynthetic responses compared to non-ASS areas (based on an analysis of a subset of 46 sites from the three groups — *Melaleuca*, 'disturbed', and *Casuarina*). Thus the low pH, high iron and higher phosphorus and nitrogen concentrations in the groundwaters from ASS areas appear very favourable to *L. majuscula* growth. The mix of dissolved nutrients in acid solution can easily be transported into waterways via groundwater flow following rainfall events (Sammut *et al.* 1996; Powell & Martens 2005). Given that ASS in the study area

Table 5. Mean (±SE) and one-way ANOVA of nutrient concentrations/properties of groundwaters collected from ASS and non-ASS areas in the Deception Bay/Bribie Island study area. Values in bold are significant, * $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$; **** $P < 0.0001$; ^{NS} non-significant.

Water property	unit	ASS areas	Non- ASS areas	F statistic
pH		**4.75 ± 0.27**	**6.04 ± 0.26**	**$F_{1,45}$ = 9.4****
Conductivity	µS cm ^{1}	**12700 ± 2850**	**1890 ± 1640**	**$F_{1,45}$ = 17.7********
Total iron	mg L ^{1}	**67.0 ± 27.0**	**3.79 ± 2.45**	**$F_{1,45}$ = 21.6********
Ferrous iron	mg L ^{1}	37.1 ± 11.8	3.36 ± 2.22	$F_{1,45}$ = 3.5^{NS}
Total phosphorus	mg L ^{1}	**0.13 ± 0.035**	**0.06 ± 0.013**	**$F_{1,45}$ = 4.8***
Phosphate	mg L ^{1}	0.03 ± 0.010	0.01 ± 0.001	$F_{1,45}$ = 1.1^{NS}
Total nitrogen	mg L ^{1}	**1.32 ± 0.21**	**0.81 ± 0.23**	**$F_{1,45}$ = 4.3***
Ammonium	mg L ^{1}	0.52 ± 0.15	0.24 ± 0.11	$F_{1,45}$ = 2.5^{NS}
NOx	mg L ^{1}	0.23 ± 0.21	0.80 ± 0.48	$F_{1,45}$ = 4.0^{NS}
DOC	mg L ^{1}	13.68 ± 1.96	8.82 ± 1.25	$F_{1,45}$ = 2.9^{NS}

commonly occur on the low-lying Holocene sediments immediately on/or adjacent to the coastline and waterways, drainage or disturbance of ASS areas would rate as a very high hazard for potentially increasing nutrients to *L. majuscula* bloom areas.

These results confirm the very high hazard rating given to iron and pH in the ASS coverage of the nutrient Hazard Model (Pointon *et al.* 2008). A high hazard rating for phosphorus, nitrogen and organics was used for actual ASS associated with wetlands while a medium hazard rating was used for phosphorus, nitrogen and organics for actual ASS not associated with wetlands (Table 4 in Pointon *et al.* (2008)).

VEGETATION

The groundwater data were grouped and analysed by dominant vegetation as land managers commonly use vegetation to discriminate differing land. Analyses of variance showed significant differences between vegetation types for groundwater conductivity, and concentrations of total iron, phosphate, ammonium and DOC (Table 4; Fig. 3).

Melaleuca. The *Melaleuca* communities of the study area (predominantly *M. quinquenervia*) typically occur in low lying areas, ranging from ephemeral wetlands to freshwater swamps. The wet and seasonally reducing conditions found in the soils of *Melaleuca* communities are favourable for the chemical reduction and cycling of iron and other nutrients (Johnston *et al.* 2003). In Florida, USA, blooms of *L. majuscula* have also occurred adjacent to large freshwater *Melaleuca* forests that yield dark stained waters (J. Burns, pers. comm.). Surface and shallow groundwaters from *Melaleuca* areas commonly have a distinctive dark 'tea' colour (Armstrong & Cox 2002), but despite this, the mean DOC concentration of waters from *Melaleuca* sites in our study areas (16 ± 2.9 mg L ^{1} C) was not as high as from wallum and pine areas (Fig. 3iii). The considerable organic matter/litter found in the surface soil below *Melaleuca* communities should contribute to complexation of iron. In our study, groundwaters from ASS *Melaleuca* sites were characterised by very low pH (mean 4.8 ± 0.38 mg L ^{1}), and the highest total iron (81 ± 50 mg L ^{1}) and ferrous iron (32 ± 19 mg L ^{1}; Fig. 2) concentrations of all vegetation groups, although this was not true of the non-ASS *Melaleuca* sites. Ahern *et al.* (2006a) found groundwaters from *Melaleuca* on both ASS ($P < 0.0001$) and non-ASS ($P < 0.05$) areas significantly stimulated *L. majuscula* productivity by 1.8 and 1.7 times the control respectively. The presence of *Melaleuca* communities in low-lying coastal areas close to waterways, combined with the lower pH and high total and ferrous iron concentrations in their groundwaters, makes such areas a likely source of nutrients to *L. majuscula* blooms.

Casuarina. Groundwaters from *Casuarina* communities were very saline (mean EC 22700 ±

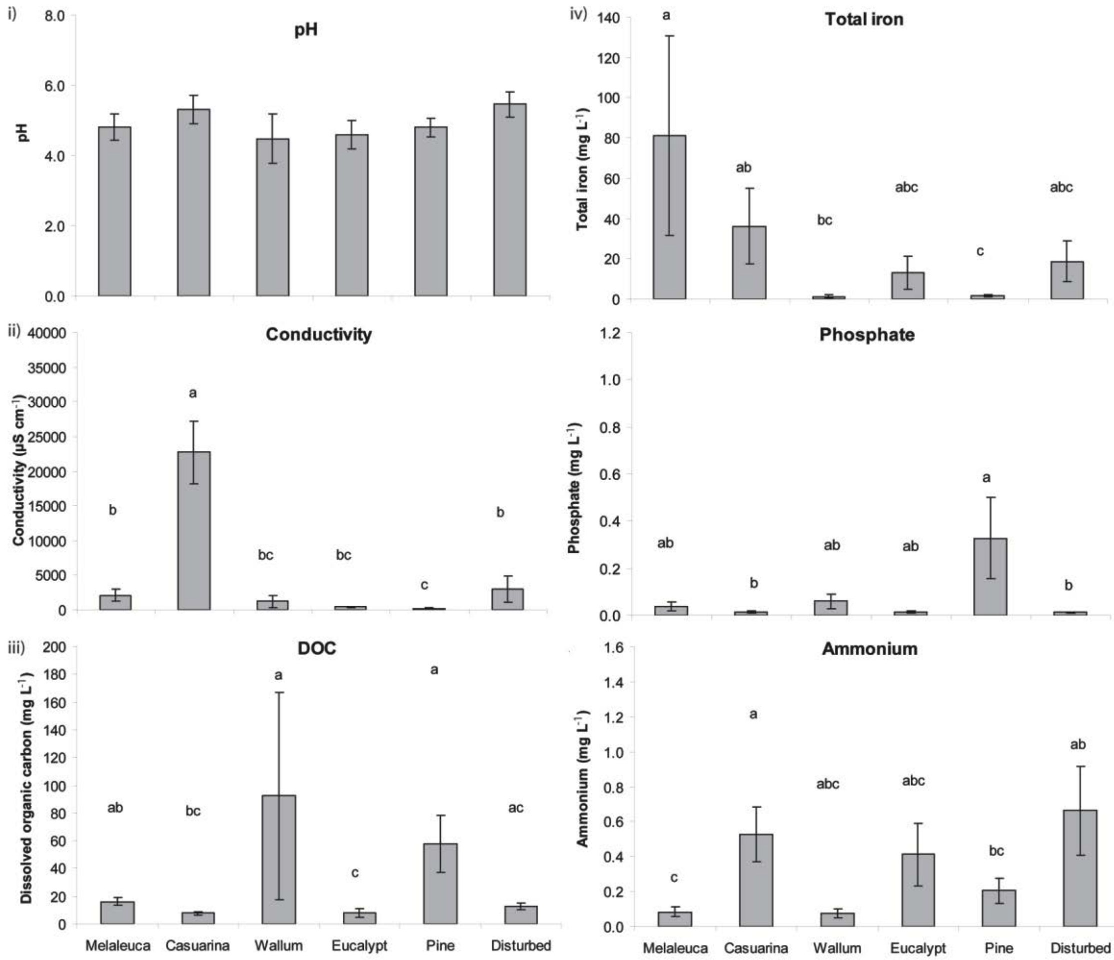

FIG. 3. Mean (±SE) of nutrient concentrations/properties of the groundwaters collected from different vegetations and disturbed landuse in the Deception Bay/Bribie Island study area : (i) pH; (ii) conductivity; (iii) DOC; (iv) total iron; (v) phosphate; and (vi) ammonium. Means followed by a common letter are not significantly different at $P > 0.05$. ANOVA for pH was not significant ($P > 0.05$).

4500 µS cm^{-1}), and had substantially higher ($P < 0.05$) conductivity than all the other vegetation classes (Fig. 3ii), reflecting their coastal locations close to watercourses and foreshores. These groundwaters were also characterised by low mean pH (5.3 ± 0.40) and relatively high mean total iron (36 ± 19 mg L^{-1}) and ferrous iron (27 ± 12 mg L^{-1}) concentrations, being second only to *Melaleuca* (Fig. 3). Ahern *et al*. (2006a) found that *Casuarina* on ASS (dominantly *C.glauca*), produced a highly significant *L. majuscula* response 2.2 times the control, whereas the non-ASS *Casuarina* (dominantly *C.cunninghamiana*) caused a response 1.5 times the control but was not statistically significant. The higher response for the *Casuarina* on ASS is likely due to lower mean pH (by a whole unit which is a factor of 10), 6 times higher mean total iron, 5 times higher ferrous iron, 1.8 times total phosphorus, 2.8 times phosphate and 1.5 times ammonium concentrations in the groundwaters, compared with *Casuarina* on non-ASS (Fig. 2).

Wallum. The wallum group (or coastal heathland) was the only group that did not elevate *L. majuscula* response compared to the control.

Wallum typically grows on acidic, highly leached, sandy, low-fertility soils, deficient in phosphorus and most trace elements (Coaldrake 1961). This was reflected in the groundwaters of the current study, which were very acidic (pH 4.48 ± 0.70) and had very low mean total iron (1.3 ± 0.74 mg L^{-1}), ferrous iron (1.7 ± 0.75 mg L^{-1}), total phosphorus (0.037 ± 0.005) and ammonium concentrations (0.07 ± 0.03 mg L^{-1}) (Fig. 3). Wallum groundwater had high DOC concentrations (92.3 ± 74.6 mg L^{-1}) but probably because of the very low nutrient concentrations, this did not elevate *L. majuscula* response.

Eucalypt. Ahern *et al.* (2006a) reported groundwaters from eucalypt communities elevated *L. majuscula* productivity by 1.3 times the control mean, but this was not statistically significant. Eucalypt vegetation is commonly located on more elevated, better drained, landscapes and thus waterlogging with associated anoxia and high nutrient bioavailability would be atypical. In the current study, the groundwaters from eucalypt communities had the lowest (or equal lowest) phosphorus, phosphate, and DOC concentrations of all the vegetation groups (Fig. 3). However, the mean total iron (13± 8.3 mg L^{-1}) and ferrous iron (10 ± 5.4 mg L^{-1}) concentrations in the groundwaters from eucalypt were higher than for the wallum and pine. This was mainly a result of high iron values from two sites which had ASS at depth, as the other six sites had very low total and ferrous iron concentrations. Interestingly, groundwaters from the two eucalypt ASS sites produced very high increases in *L. majuscula* response (1.6 and 2.1 times the control). Had these two sites not been included in the eucalypt group, the mean *L. majuscula* response would likely have been closer to that of control and the walum. Thus, there appears to be no significant nutrient hazard associated with the eucalypt communities except where they grade onto the lower elevations with ASS at depth.

Pine. Ahern *et al.* (2006a) found the groundwaters from both pine groups (Bribie Island and mainland) significantly ($P < 0.01$; $P < 0.05$) stimulated *L. majuscula* response, with low pH (4.81 ± 0.27), high DOC (58 ± 21 mg L^{-1}) and relatively high total phosphorus (0.23 ± 0.12 mg L^{-1}) and phosphate (0.32 ± 0.32 mg L^{-1}) concentrations being probably responsible (Fig. 3). However, groundwaters from Bribie produced a higher response (1.9 times the control, $P < 0.01$), than those from the mainland (1.6 times, $P < 0.05$). In the present study we found that 'pine on Bribie Island' had significantly and substantially higher mean total phosphorus (15.6 times), phosphate (100 times), nitrogen (4.3 times) and ammonium (5.4 times) concentrations compared to 'pine on the mainland' (Table 6). Another study (Driscoll 2002) found higher phosphorus concentrations in groundwaters under pine plantation on Bribie compared to adjoining undisturbed 'non-pine' sites, and he suggested this was probably due to fertiliser application at planting. The sandy Podosols beneath the pine plantations on Bribie have high permeability in the upper part of the profile allowing leaching of fertiliser into the often perched shallow groundwaters. The extremely low pH (mean 3.78) also probably contributes to the effective leaching of phosphorus fertiliser into the shallow groundwater. In comparison, 'pine on mainland' had a mean pH 1.7 units higher. Very low pH conditions also favour the dissolution and leaching of other soil constituents, such as iron, aluminium and organics. These may form indurated or cemented sand layers (referred to as 'coffee rock') at the relatively shallow depths of the watertable interface. Coffee rock layers are widely distributed on Bribie Island (Armstrong & Cox 2002).

'Pine on Bribie' had 17 times higher mean DOC (133 mg L^{-1}) in the groundwaters than the mainland (Table 6), and were described by Armstrong & Cox (2002) as dominantly 'black' in colour. Such a high DOC is usually associated with shallow perched groundwater over coffee rock (Armstrong & Cox 2002), and this also leads to waterlogging, anoxia, and high nutrient bioavailability. At 'pine on the mainland' sites such indurated layers are uncommon. Organic matter/DOC from pine extracts has been found to have very strong iron complexing properties compared to organics from native vegetations such as *Acacia* and wallum (Rose & Waite 2003). The combination of high rainfall on sandy soils, and the relatively shallow, impermeable layers and perched watertables on Bribie Island, results in lateral movement of shallow groundwaters

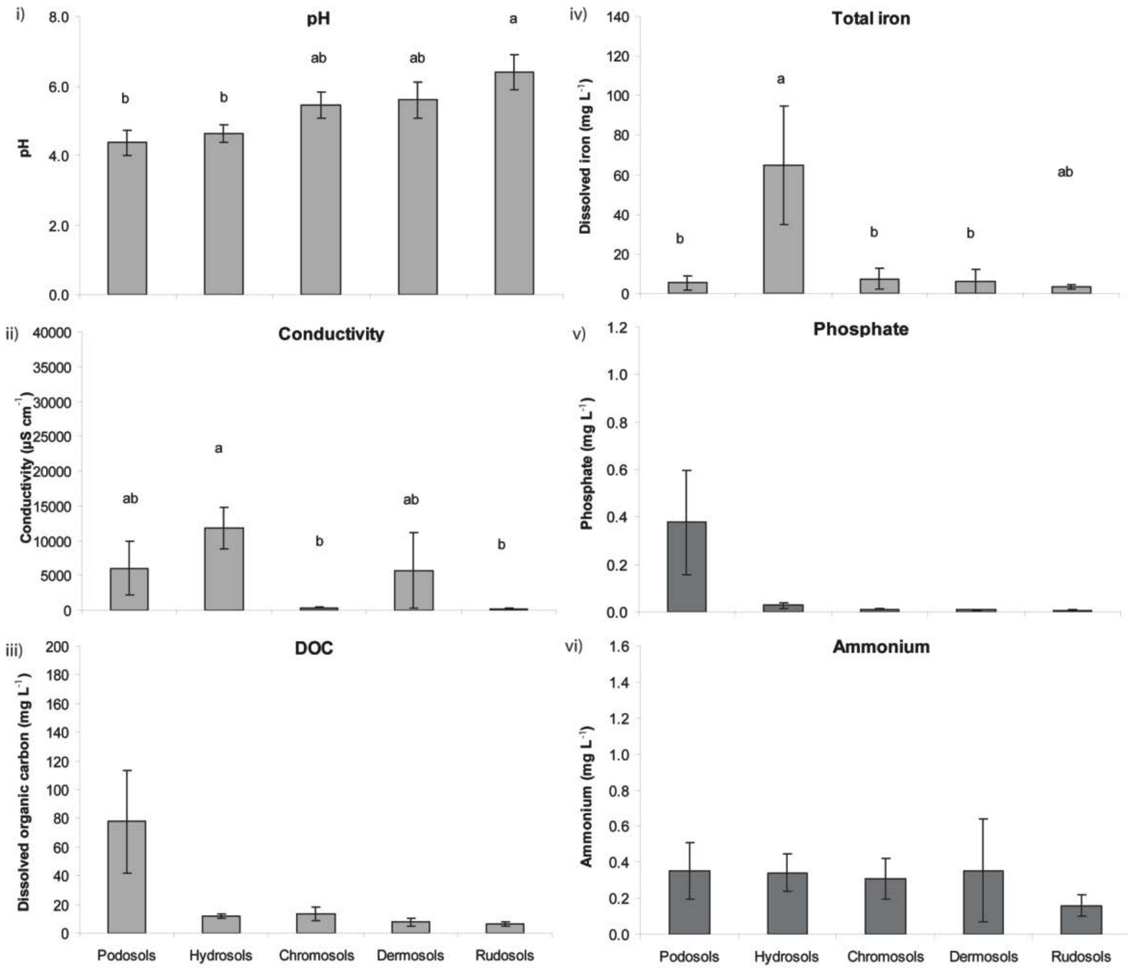

FIG. 4. Mean (±SE) of nutrient concentrations and properties of the groundwaters collected from different soil orders in the Deception Bay/Bribie Island study area: (i) pH; (ii) conductivity; (iii) DOC; (iv) total iron; (v) total phosphorus; and (vi) ammonium. Means followed by a common letter are not significantly different at $P > 0.05$. ANOVA for DOC and ammonium were not significant ($P > 0.05$).

(rich in DOC and phosphorus) into surrounding waterways (Armstrong & Cox 2002). Thus pine plantations (particularly on Bribie), are a potentially important source of nutrients to *L. majuscula* blooms.

SOIL ORDER GROUPINGS

Our study showed highly significant differences in the nutrient concentrations and properties of the groundwaters (Table 4; Fig. 4) from the five main Australian Soil Classification orders (Isbell 1996) in the Deception Bay/Pumicestone Passage area, and thus, consequent differences in their intrinsic potential to store and supply nutrients needed for *L. majuscula* growth.

Podosols. Podosols are defined as soils with the B horizon dominated by the accumulation of compounds of organic matter, aluminium and/or iron (Isbell 1996), and include indurated sands or 'coffee rock'. *L. majuscula* has been observed growing on coffee rock where it has been exposed under the sea at Fraser Island (Dennison *et al.* 1999). Groundwaters from Podosols in the current study (Fig. 4) had mean total iron concentration of 5.3 ± 3.5 mg L ^{1} Fe, with a high proportion in the ferrous form (4.9 ± 3.1 mg L ^{1}

Table 6. Mean (±SE) and one-way ANOVA of groundwaters nutrient concentrations/properties collected from pine plantations on the mainland and pine plantations on Bribie Island. Values in bold are significant, * $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$; ^{NS} non-significant.

Water property	**units**	**Pine (Bribie Is.)**	**Pine (mainland)**	***F* statistic**
Conductivity	µS cm ^{1}	**313 ± 58**	**142 ± 23**	**$F_{1,13}$ = 12.2****
pH		**3.78 ± 0.10**	**5.49 ± 0.25**	**$F_{1,13}$ = 28.1*****
Total iron	mg L ^{1}	2.73 ± 1.32	1.12 ± 0.55	$F_{1,13} = 1.8^{NS}$
Ferrous iron	mg L ^{1}	2.91 ± 1.22	1.78 ± 0.98	$F_{1,13} = 3.5^{NS}$
Total phosphorus	mg L ^{1}	**0.71 ± 0.30**	**0.05 ± 0.006**	**$F_{1,13}$ = 7.0***
Phosphate	mg L ^{1}	**0.81 ± 0.36**	**0.008 ± 0.002**	**$F_{1,13}$ = 18.7*****
Total nitrogen	mg L ^{1}	**2.81 ± 0.67**	**0.66 ± 0.10**	**$F_{1,13}$ = 8.5***
Ammonium	mg L ^{1}	**0.40 ± 0.14**	**0.07 ± 0.04**	**$F_{1,13}$ = 11.5****
NOx	mg L ^{1}	0.05 ± 0.02	0.03 ± 0.02	$F_{1,13} = 2.8^{NS}$
DOC	mg L ^{1}	133 ± 34	7.68 ± 1.3	$F_{1,13} = 3.5^{NS}$

Fe). This is similar to the mean iron levels of other soil orders with the exception of the Hydrosols which had 7 times more ferrous iron and 12 times more total iron than the Podosols. Podosols are commonly highly acidic (Isbell 1996) which was certainly the case in the current study as groundwaters from these soils had the lowest mean pH (4.4 ± 0.35) of all the soil classes in the study area, being significantly ($P < 0.05$) lower than the Rudosols by 2 pH units.

The mean total phosphorus (0.175± 0.036 mg L ^{1}) in groundwaters from Podosols was the highest of all soil orders. The mean phosphate concentrations were significantly ($P > 0.05$) higher than all other soils, but we attribute this to their association with pine plantations that receive fertiliser application at planting. The Podosols also had the highest mean total nitrogen and ammonium values of all the soils, but differences were not statistically significant. Mean DOC concentrations (78 ± 36 mg L ^{1}) were substantially (>5 times) higher than for other soil orders but also not significant ($P > 0.05$), and probably influenced by pine plantation sites (particularly from Bribie) with perched watertables. Perched watertable levels vary widely with season, although the near coastal Podosols, particularly on Bribie, receive more regular top-up from coastal rain. Lateral movement of nutrient-rich perched groundwater via the sandy surface soils to streams and the near shore marine environment, is both likely and of concern.

Hydrosols. Hydrosols include a range of seasonally or permanently wet soils, with saturation of the greater part of the profile for prolonged periods (2–3 months), in most years, necessary for their classification (Isbell 1996). Groundwaters were characterised by high conductivity, very low mean pH (4.6 ± 0.26), and the highest mean total iron (65 ± 30 mg L ^{1}) and ferrous iron (35 ± 12 mg L ^{1}) concentrations of the soil orders (Fig. 4). The significantly higher ($P < 0.05$) mean conductivity (11751 ± 3004 µS cm ^{1}) reflects current or historical marine inundation. The high iron is probably from reducing and oxidative conditions for part of the year, manifested as 'gley' colours and ochrous mottles (Isbell 1996), and many sites are also ASS. As Hydrosols are typically low lying, with groundwaters closer to the surface for at least part of the year, they support more vegetation and have higher nutrient levels than other drier, higher, soil types. Thus, disturbance or drainage of Hydrosols is likely to lead to nutrient export to adjacent waterways.

Chromosols. Chromosols have a strong texture contrast between the topsoil (A horizon) and subsoil (B horizon) (Isbell 1996). In the present study the mean groundwater pH was acidic (pH = 5.45 ± 0.37), while conductivity was very low (197 ± 73 µS cm ^{1}) indicating almost fresh water (Fig. 4). The NOx concentrations were the highest (mean 10 ± 9 mg L^{1}) of all the soil orders. Chromosols are predominantly used for agricultural/horticultural production in the study area and so are subject to nitrogenous fertilisation — particularly where pineapples are grown.

Dermosols. Dermosols are soils with structured B2 horizons that lack strong texture contrast between A and B horizons; they also have high agricultural potential with good structure, and moderate to high chemical fertility and water-holding capacity (Isbell 1996). In our study area their groundwaters had a mean pH of 5.6 ± 0.52, similar to the Chromosols (Fig. 4). Mean conductivity was similar to the Podosols at about 0.1 times that of seawater (5740 ± 5420 µS cm^{1}), but more saline groundwaters occurred closer to the coast.

Rudosols. Rudosols are typically young soils with negligible pedologic organisation, meaning that insufficient time has passed for the colour, texture, or structure of the parent rock or sediments to be significantly modified (Isbell 1996). This was reflected in the low nutrient content of the groundwaters that contained the lowest (or about equal lowest) mean ferrous iron, total iron, phosphate, total phosphorus, ammonium, NOx, total nitrogen and DOC concentrations of all the soil groups (Fig. 4). The mean pH of the groundwaters from these soils was the closest to neutral (6.4 ± 0.5) of all the soils groups, and significantly ($P < 0.05$) higher than the pH of Hydrosols and Podosols. Conductivity was very low (200 ± 73µS cm^{1}) indicating nearly fresh water.

GEOLOGY

Analyses of variance of the groundwaters from the three main geology groupings [marine, alluvium and continental] sampled in the Deception Bay/Pumicestone Passage area, showed significant differences between groups for conductivity, pH, ferrous iron, total iron, ammonium nitrogen, total nitrogen and DOC (Table 4; Fig. 5).

The marine group had mean groundwater conductivity 38 times higher than the alluvium group (significant at $P < 0.001$), and 68 times the continental group (Fig. 5) , reflecting strong residual salinity from their marine origin. The continental group, with the lowest mean conductivity, consists mainly of the *Landsborough Sandstone* formation originally formed from the accumulation of terrestrial sediments (where the salt content of the sandstone was inherently low). Though the alluvium group also had higher mean conductivity than the continental group, this was not statistically significant.

The marine group had much lower mean pH (4.61 ± 0.2) than the continental group (5.46 ± 0.32) and significantly ($P < 0.001$) so for the alluvium group (pH= 5.98 ± 0.24) (Fig. 5). The very low mean pH of the marine group is mainly attributed to areas with oxidation of iron sulfide in the ASS common to this group (though potential ASS that has not begun to oxidise, or is under the tidal influence of seawater, would be expected to be similar to seawater i.e. neutral to slightly alkaline). Other very low pH soils in this group include the coastal sandy soils (mainly Podosols) supporting pine plantations on Bribie Island.

The mean ferrous iron concentration from the marine areas was significantly ($P < 0.01$) greater (8.6 times) than the alluvium group, and 22 times greater than the continental group, though not significant on the latter. The mean total iron concentration of the Marine group was significantly ($P < 0.001$) greater (18 times) than the alluvium group, and 35 times greater than the continental group ($P < 0.05$). The ASS in the marine group are largely responsible for these higher iron concentrations.

The mean ammonium concentration of the marine group was significantly ($P < 0.05$) higher than the continental group (by 4.9 times), and almost double that of the alluvium group though this was not significant. The mean NOx levels of the marine group was less than a third of the other two groups, although all levels were quite low (Fig. 5). This suggests that the groundwaters from the marine group usually experience lower redox conditions than the other groups. Marine group soils are usually located in the lowest landscape positions, and many sites (particularly with ASS) may be waterlogged for at least a few months of the year — hence more reduced than the better drained alluvium and continental groups. The mean total nitrogen of the marine group was significantly ($P < 0.01$) greater (2.8 times) than the alluvium group, and 1.6 times the continental group, though not significant for the latter.

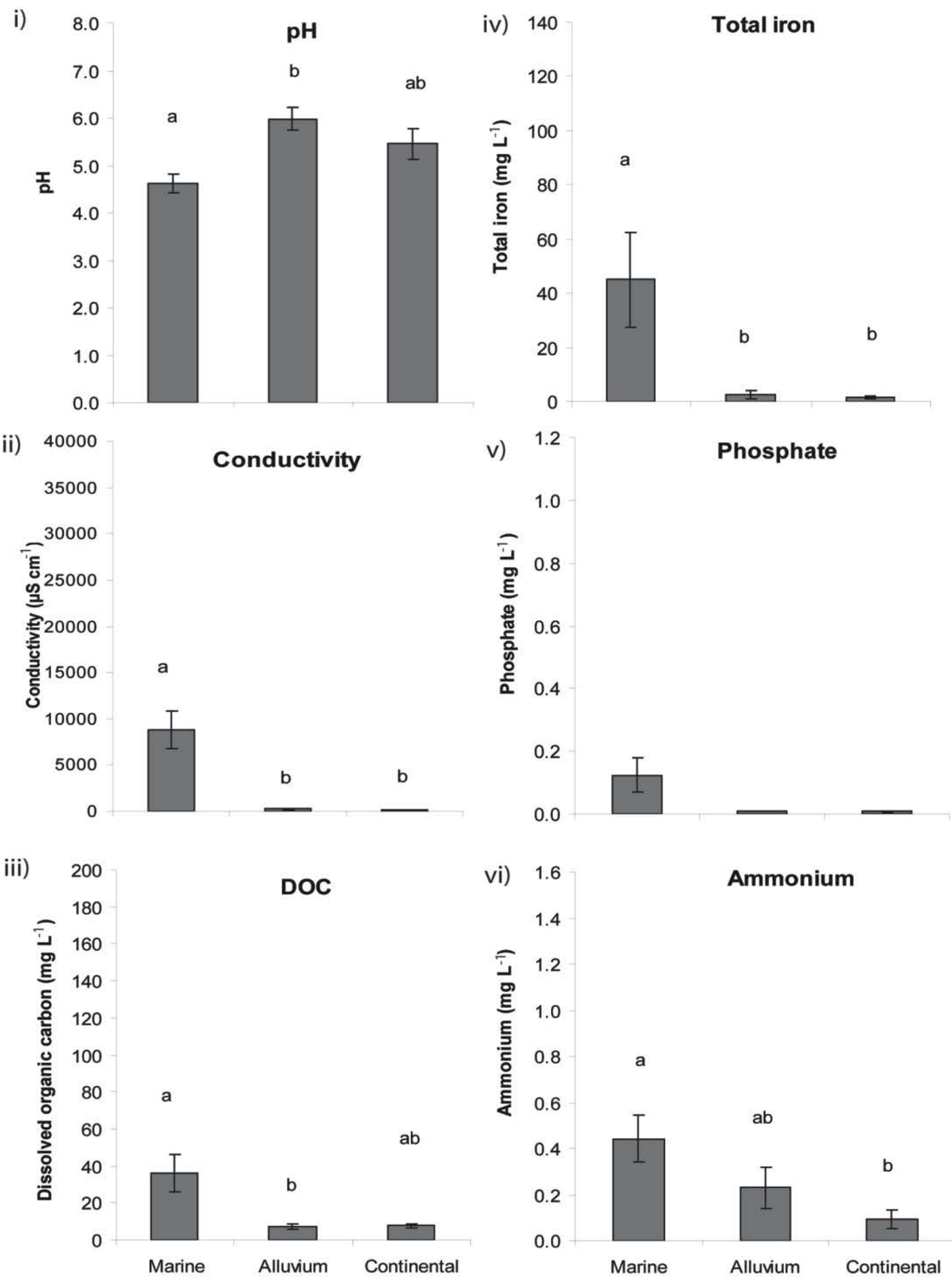

FIG. 5. Mean (±SE) of nutrient concentrations and properties of the groundwaters collected from different geologies in the Deception Bay/Bribie Island study area: (i) pH; (ii) conductivity; (iii) DOC; (iv) total iron; (v) total phosphorus; and (vi) ammonium. Means followed by a common letter are not significantly different at $P > 0.05$.

APPLICATION FOR MODELLING

The outcomes of the present study confirm the efficacy of the *Lyngbya majuscula* nutrient 'Hazard Model', support its further refinement, and assist with hazard ratings. This model was created to identify, and rate, different areas, in terms of how likely/vulnerable they are to supply and export nutrients that could increase the likelihood and magnitude of *L. majuscula* blooms in southeast Queensland (Pointon *et al.* 2008). The map outputs from earlier versions of the Hazard Model have helped to identify areas needing further assessment (EPA 2006). The eventual aim is to incorporate nutrient hazard maps into local government planning schemes.

NUTRIENTS AND PROPERTIES

Increases in iron and phosphorus were directly and significantly correlated with *L. majuscula* photosynthetic response, and both were significant dependant variables in the multiple regression. Thus our data support the inclusion of both nutrients in the risk-rating process. This is further supported by other laboratory and *in situ* studies that have shown similar responses to additions of organically chelated iron (Gross & Martin 1996; Dennison *et al.* 1999; Ahern *et al.* 2006b) and/or phosphorus (Kuffner & Paul 2001; Elmetri & Bell 2004; Ahern *et al.* 2007a).

The inclusion of pH in the risk-rating process is also supported. Groundwater pH was a significant dependant variable in the multiple regression of *L. majuscula* photosynthetic response. pH was initially included in the hazard rating process of the Hazard Model because of its known affect on the solubility and hence the movement and bioavailability of iron and phosphorus. In this study, the generally greater solubility of iron with low pH led to a negative correlation between total iron and pH, i.e. the more acidic waters generally had the highest total iron contents.

With regard to nitrogen, the significant correlation of *L. majuscula* productivity with ammonium concentrations supports its inclusion in the Hazard Model. However, despite being shown in this and other studies (Ahern *et al.* 2007a; Ahern *et al.* 2008) that growth is stimulated by additions of inorganic nitrogen, *L. majuscula* can also fix atmospheric nitrogen (Lundgren *et al.* 2003), and is therefore not necessarily completely reliant on an external inorganic nitrogen source.

The results for dissolved organic carbon emphasise the complex relationships between DOC and *L. majuscula* response, especially when different organic sources of DOC are involved. While there were significant correlations of DOC with total nitrogen, total phosphorus, and phosphate, measuring the concentrations of DOC alone, without measuring the strength of complexing properties was not predictive of a *L. majuscula* response. None-the-less, the inclusion of DOC in the Hazard Model is partly justified given that DOC (sourced from the Deception Bay/Pumicestone Passage catchment) has been shown to strongly complex iron and thus reduce its precipitation in seawater (Rose & Waite 2002; Rose & Waite 2003). Measurement of the DOC complexing strength with iron (and phosphorus) for a much wider range of landuses/vegetation/soil/geology in the catchment, may improve its usefulness in the Hazard Model, as only a limited number of organic sources have been tested for complexing strength (Rose & Waite 2002; Rose & Waite 2003).

Although conductivity was a significant dependant variable in the multiple regression, any suggestion that it would directly cause an *L. majuscula* response is unsupported, and there is no justification for its inclusion in the Hazard Model.

VEGETATION, SOILS, GEOLOGY AND LANDUSES AS SIMPLE RISK IDENTIFIERS

Some areas within the catchment characterised by differing vegetation, soils, geology and landuse, also differ in their potential to supply nutrients to the waterways. Areas with ASS, *Melaleuca* vegetation, pine plantations, *Casuarina* on ASS, Hydrosols, Podosols and 'marine influenced geology' all have groundwaters that directly increase *L. majuscula* response in bioassays, or that contain significant quantities of nutrients likely to cause this response. The importance of careful management of such recognisable parcels of land should be communicated to landholders, particularly as it does not require the more complex explanations associated with the Hazard Model.

In addition, areas with some of the following characteristics may be important contributors of nutrients to *L. majuscula* blooms if subject to disturbance or alteration, and should be rated medium to high hazard in the Hazard Model:

- Areas that contain appreciable concentrations of iron, phosphorus and/or nitrogen, or where management involves application of organic or inorganic fertilisers;
- Areas where site conditions (e.g. waterlogging and anaerobic conditions, perched groundwater tables) promote formation of nutrients into bioavailable form;
- Areas where the site conditions readily promote transport of nutrients to waterways (e.g. highly transmissive, permeable soils with perched watertables, such as Podosols on Bribie).

Obviously, if such areas are also situated close to waterways and coastlines (e.g. ASS areas, *Melaleuca* wetlands), they are likely to be a still greater hazard. This was taken into account in the Hazard Model by the use of proximity to coast and streams layers.

A limitation of the current study was that it could only test and examine groundwaters from a limited number of different landuses/vegetations/soils combinations. Although those combinations tested were very relevant, as they included many 'higher risk' practices as well as spatially extensive areas of the catchment (e.g. pine plantations), further testing of other combinations of soils, vegetations and landuses present in the study area are needed. Furthermore, more testing is required when extending the Hazard Model beyond the 'reference area' used in this study to other coastal areas of Southeast Queensland.

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