11-9-2005

Ammonium Distribution and Dynamics in Relation to Biological Production and Physical Environment in the Marguerite Bay Region of the West Antarctic Peninsula

Yulia Mikhailovna Serebrennikova

University of South Florida

Follow this and additional works at: https://scholarcommons.usf.edu/etd

Part of the American Studies Commons

Scholar Commons Citation

This Dissertation is brought to you for free and open access by the Graduate School at Scholar Commons. It has been accepted for inclusion in Graduate Theses and Dissertations by an authorized administrator of Scholar Commons. For more information, please contact scholarcommons@usf.edu.
Ammonium Distribution and Dynamics in Relation to Biological Production and Physical Environment in the Marguerite Bay Region of the West Antarctic Peninsula

by

Yulia Mikhailovna Serebrennikova

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy
College of Marine Science
University of South Florida

Major Professor: Kent Fanning, Ph.D.
John J. Walsh, Ph.D.
Kendra L. Daly, Ph.D.
Gabriel A. Vargo, Ph.D.
James M. Krest, Ph.D.

Date of Approval:
November 9, 2005

Keywords: antarctic nutrient cycle, nutrient utilization, net community production, nutrient regeneration, simulation model

© Copyright 2006, Yulia Serebrennikova
Acknowledgments

I thank my major professor Dr. Kent Fanning and committee members Drs. John Walsh, Gabriel Vargo, Kendra Daly, and James Krest. I would also like to thank Dr. J. Walsh and Dwight Dieterle for providing the model and help with the interpretation of the results. Additionally, I thank Maria Vernet of Scripps Institute of Oceanography, Robin Ross and Langdon Quetin of Marine Science Institute of University of California, Carin Ashjian, Philip Alatalo, and Jason Hyatt of Woods Hole Oceanographic Institute, Kendra Daly of University of South Florida, and John Dore of University of Hawaii for sharing their data. I also thank fellow nutrient team members Rob Masserini, Howard Rutherford, Rebecca Conroy, and Steve Bell for obtaining the highest quality nutrient data set for the SO GLOBEC program.
Table of Contents

List of Tables iii
List of Figures v
Abstract xi

1. Introduction 1
   1.1. Ammonium in the Ocean 1
   1.2. General characteristics of the area 11
   1.3. Field sampling design and schedule 12

2. Biogeochemical Regimes 15
   2.1. Introduction 15
   2.2. Hydrographic and physicochemical properties in 2001 and 2002 15
   2.3. Nutrient deficit calculations 39
   2.4. Nutrient deficits in 2001 and 2002 44
      2.4.1. Nutrient deficits in January of 2001 44
      2.4.2. Nutrient deficits in April-May of 2001 50
      2.4.3. Nutrient deficit in July-August of 2001 57
      2.4.4. Nutrient deficit in September-October of 2001 59
      2.4.5. Nutrient deficit in January of 2002 61
      2.4.6. Nutrient deficit in April-May of 2002 66
      2.4.7. Nutrient deficit in August-September of 2002 69
   2.5. Net community production in 2001 and 2002 74
   2.6. Nutrient utilization ratios 85
   2.7. Seasonal variability in nutrient deficits 88
   2.8. Summary 89

3. Ammonium 92
   3.1. Ammonium stocks distribution in 2001 and 2002 92
   3.2. Nitrite dynamics in the Marguerite Bay region in 2001 and 2002 103
   3.3. Ammonium sources 104
   3.4. Regeneration 113
   3.5. Seasonal variability in ammonium 115
   3.6. Summary 120

4.1. Introduction

4.2. Model description

4.2.1. Vertical mixing

4.2.2. Lateral mixing

4.2.3. Boundary and initial conditions

4.2.4. State equations

4.2.4.1. Phytoplankton

4.2.4.2. Zooplankton: grazing and excretion

4.2.4.3. Protozoa dynamics

4.2.4.4. Microbial loop dynamics

4.2.4.5. Dissolved inorganic pool

4.2.5. Model implementation

4.3. Modeling results

4.3.1. Time evolution of nitrate and ammonium in Marguerite Bay in 2000-2001 and 2001-2002 seasons

4.3.2. Phytoplankton stocks dynamics in Marguerite Bay during the 2000-2001 and 2001-2002 seasons

4.3.3. Simulated dissolved organic carbon and bacterial dynamics in Marguerite Bay during the 2000-2001 and 2001-2002 seasons

4.3.4. Ammonium production in Marguerite Bay during the 2000-2001 and 2001-2002 seasons

4.3.5. Nitrification as a sink for ammonium in Marguerite Bay during the 2000-2001 and 2001-2002 seasons

4.3.6. Modeling the nutrient changes in Marguerite Bay between 2000-2001 and 2001-2002

4.3.7. Sensitivity analysis

4.4. Model conclusions

References

About the Author
List of Tables

Table 1. A compilation of SO LTER and GLOBEC survey designations, dates, and stations for the 2001 and 2002 field seasons. 14
Table 2. Averages and ranges for the vertical stability of the mixed layer and mixed layer depth for summer, autumn and winter time surveys in 2001 and 2002. 19
Table 3. The remnant WW layer properties in the study region including the average depth of the layer, the range in silica concentration and the values (mean ± 2S.D.) of salinity, phosphate, and total inorganic nitrogen (TIN=[NO₃]+[NO₂]+[NH₄]) observed in the layer in summers and autumns of 2001 and 2002. 41
Table 4. Averages and ranges for the deficits of total inorganic nitrogen (TIN), phosphate, silica and Net community production (NCP) estimates integrated to the depths of the remnant WW layer for summer, autumn, and winter time surveys in 2001 and 2002. 45
Table 5. Averages and ranges for the deficits of total inorganic nitrogen (TIN), phosphate, silica and Net community production (NCP) estimates from the summer and autumnal 1997 JGOFS survey in the Ross Sea, which are reported in Sweeney et al. (2000b) and from the summer data of the southern Pacific, which are reported in Rubin et al. (1998). 84
Table 6. Averages and ranges for the ammonium (NH₄ST) and nitrite (NO₂ST) stocks for summer, autumn and winter time surveys in 2001 and 2002. 96
Table 7. Average deficits of total inorganic nitrogen (Def(TIN)), phosphate (Def(PO₄)), and silica (Def(SIL)), Net community production (NCP) and ammonium stocks (NH₄ST) for Marguerite Bay (Marguerite Bay is defined as the area between Adelaide and Alexander Islands and the coast of Antarctic Peninsula (Fig. 1)) in autumns of 2001 and 2002. 124

Table 9. The initial and boundary conditions of ammonium (µM), nitrate (µM), dissolved inorganic carbon (µM), diatom (D), nanoflagellate (NF) and prymnesiophytes (Pr) groups of phytoplankton (mg chl a m⁻³), bacteria (mg C m⁻³), and refractory background (DOCᵣ) and labile (DOC₁,₂) dissolved organic carbon (µM) within Marguerite Bay.

Table 10. Model parameters of Marguerite Bay plankton communities.

Table 11. Monthly average maximal grazing stress (mg C m⁻² d⁻¹) on diatoms during the (a) 2000-2001 and (b) 2001-2002 seasons.

Table 12. Four cases of model’s responses in terms of ammonium concentration to changes of zooplankton and bacterial biomass.

Table 13. Sensitivity of the selected model results (maximum chlorophyll concentration (mg chl a m⁻³), maximal bacterial biomass (mg C m⁻³), minimal nitrate concentration (µM), maximal ammonium concentration (µM), annual primary production (PP) of POC (g C m⁻² yr⁻¹), and Net community production (NCP) (mol N m⁻²) ) to perturbation of each parameter by ±50% of its value for 2000-01 and 2001-02 model scenarios.
List of Figures

Figure 1. Map of Marguerite Bay (MB) and the adjacent WAP continental shelf. 7

Figure 2. Distribution of physicochemical properties in January of 2001. 17

Figure 3. Distribution of physicochemical properties in April-May of 2001. 20

Figure 4. Distribution of physicochemical properties in July-August of 2001. 23

Figure 5. Distribution of physicochemical properties in January of 2002. 25

Figure 6. Distribution of physicochemical properties in April-May of 2002. 28

Figure 7. Distribution of physicochemical properties in August-September of 2002. 30

Figure 8. Temperature (°C) distribution at temperature minimum level in (a) January of 2001, (b) April-May of 2001, (c) January of 2002, and (d) April-May of 2002. 32

Figure 9. Distribution of potential temperature (°C) maximum below 200 m in (a) January of 2001, (b) April-May of 2001, (c) July-August of 2001, (d) January of 2002, (e) April-May of 2002, and (f) August-September of 2002. 35

Figure 10. Illustration to the deficit calculation technique on example of TIN deficit calculation at a station inside Marguerite Bay. 40

Figure 11. (a) Distribution of Def (TIN), mol m$^{-2}$, (b) Def (SIL), mol m$^{-2}$, (c) ΔN/ΔP ratio, and (d) ΔSi/ΔN ratio in January of 2001. 46

Figure 12. (a) The relationships between Def (TIN) and Def (PO$_4$) for January of 2001. 48

Figure 13. Distribution of pigment averaged over the euphotic zone in January of 2001. 51

Figure 14. (a) Distribution of Def (TIN), mol m$^{-2}$, (b) Def (SIL), mol m$^{-2}$, (c) ΔN/ΔP ratio, and (d) ΔSi/ΔN ratio in April-May of 2001. 53
Figure 15. (a) The relationships between $\text{Def} (\text{TIN})$ and $\text{Def} (\text{PO}_4)$ for April-May of 2001.

Figure 16. (a) Distribution of $\text{Def} (\text{TIN})$, mol m$^{-2}$ and (b) $\text{Def} (\text{SIL})$, mol m$^{-2}$ in July-August of 2001.

Figure 17. Vertical sections of the distribution of (a) potential temperature ($^\circ$C), (b) salinity, and (c) nitrate concentration ($\mu$M) along transect #2 (see Fig. 1c for the location) in July-August of 2001.

Figure 18. (a) The relationships between $\text{Def} (\text{TIN})$ and $\text{Def} (\text{PO}_4)$ for July-August of 2001.

Figure 19. (a) Distribution of $\text{Def} (\text{TIN})$, mol m$^{-2}$ and (b) $\text{Def} (\text{SIL})$, mol m$^{-2}$ in September-October of 2001.

Figure 20. (a) Distribution of $\text{Def} (\text{TIN})$, mol m$^{-2}$, (b) $\text{Def} (\text{SIL})$, mol m$^{-2}$, (c) $\Delta N/\Delta P$ ratio, and d) $\Delta Si/\Delta N$ ratio in January of 2002.

Figure 21. (a) The relationships between $\text{Def} (\text{TIN})$ and $\text{Def} (\text{PO}_4)$ for January of 2002.

Figure 22. (a) Distribution of the $\text{Def} (\text{TIN})$, mol m$^{-2}$, (b) $\text{Def} (\text{SIL})$, mol m$^{-2}$, (c) $\Delta N/\Delta P$ ratio, and d) $\Delta Si/\Delta N$ ratio in April-May of 2002.

Figure 23. (a) The relationships between $\text{Def} (\text{TIN})$ and $\text{Def} (\text{PO}_4)$ for April-May of 2002.

Figure 24. (a) Distribution of $\text{Def} (\text{TIN})$, mol m$^{-2}$ and (b) $\text{Def} (\text{SIL})$, mol m$^{-2}$ in August-September of 2002.

Figure 25. (a) The relationships between $\text{Def} (\text{TIN})$ and $\text{Def} (\text{PO}_4)$ for August-September of 2002.

Figure 26. Vertical sections of the distribution of (a) potential temperature ($^\circ$C), (b) salinity, and (c) nitrate concentration ($\mu$M) along transect #2 (see Fig. 1g for the location) in August-September of 2002.

Figure 27. Distribution of (a) average euphotic zone chlorophyll $a$ concentration (mg m$^{-3}$) and (b) average euphotic zone phaeopigment concentration (mg m$^{-3}$) in January of 2001.

Figure 28. Distribution of chlorophyll $a$ concentration averaged over the upper 50 m of the water column (mg m$^{-3}$) in April-May of 2001.
Figure 29. Distribution of (a) average euphotic zone chlorophyll $a$ concentration (mg m$^{-3}$) and (b) average euphotic zone phaeopigment concentration (mg m$^{-3}$) in January of 2002.

Figure 30. Distribution of chlorophyll $a$ concentration averaged over the upper 50 m of the water column (mg m$^{-3}$) in April-May of 2002.

Figure 31. Sea ice extent and concentration (%) in Marguerite Bay (MB) and the adjacent part of the WAP continental shelf for 15th day of each month from November of 2000 to June of 2001 as derived from Special Sensor Microwave Imager (SSM/I) satellite data (data were courtesy of J. Hyatt (WHOI)).

Figure 32. Sea ice extent and concentration (%) in Marguerite Bay (MB) and the adjacent part of the WAP continental shelf for 15th day of each month from November of 2001 to June of 2002 as derived from Special Sensor Microwave Imager (SSM/I) satellite data (data were courtesy of J. Hyatt (WHOI)).

Figure 33. Vertical distribution of ammonium concentration ($\mu$M) on (a) line 200 in January of 2001, (b) transect 5 in April-May of 2001, (c) line 200 in January of 2002, and (d) transect 5 in April-May of 2002.

Figure 34. Distribution of ammonium stocks in (a) January of 2001, (b) April-May of 2001, (c) July-August of 2001 (Letters indicate the regions of low (A2) and high (B2 and C2) ammonium stocks), (d) January of 2002, (e) April-May of 2002 (Letters A3-C3 indicate the regions of high ammonium stocks), (f) August-September of 2002. All units are in mol m$^{-2}$.

Figure 35. Distribution of the macrozooplankton biomass collected from 2-m$^2$ metro trawl towed obliquely between the surface and 120 m in January of 2001.

Figure 36. Relationship between the average euphotic zone chlorophyll $a$ concentration (mg m$^{-3}$) and silica deficit (mol m$^{-2}$) in January of 2001.

Figure 37. Distribution of the macrozooplankton biomass collected from 2-m$^2$ metro trawl towed obliquely between the surface and 120 m in January 2002.

Figure 38. Relationship between salinity and ammonium concentration ($\mu$M) in the mixed-layer.
Figure 39. Vertical distribution of (A) chlorophyll $a$ (mg m$^{-3}$), (B) nitrate ($\mu$M), (C) ammonium ($\mu$M), and D) nitrite ($\mu$M) concentrations along the transect perpendicular to the retreating ice edge during RACER 3 cruise to Marguerite Bay (Dore et al., 1992).

Figure 40. A model structure of the cycles of carbon and nitrogen between pools of atmospheric and marine carbon dioxide, nitrate, ammonium, three competing groups of phytoplankton (diatoms, cryptophytes, and prymnesiophytes), major zooplankton (krill, copepods, and protozoa), bacteria, zooplankton fecal pellets, monomeric (DOC$_1$) and macromolecular (DOC$_2$) dissolved organic carbon regulated by availability of light and mixing regime in Marguerite Bay.

Figure 41. The model’s annual cycles of (a) nitrate ($\mu$M) and (b) ammonium ($\mu$M) during 2000-2001 scenario and (c) nitrate ($\mu$M) and (d) ammonium ($\mu$M) during 2001-2002 scenario in Marguerite Bay.

Figure 42. (a) Vertical profile of nitrate concentration ($\mu$M) at a LTER station in Marguerite Bay (see Fig. 1a for location) during January 2001.

Figure 43. Simulated time series of total DIN, nitrate, and ammonium uptake by phytoplankton (mmol N m$^{-2}$ d$^{-1}$) in Marguerite Bay for (a) 2000-2001 and (b) 2001-2002 scenarios.

Figure 44. (a) Vertical profile of ammonium concentration ($\mu$M) at a LTER station in Marguerite Bay (see Fig. 1a for location) during January 2001.

Figure 45. The model’s annual cycles of biomass (mg chl $a$ m$^{-3}$) of (a) total chlorophyll, (b) diatoms, (c) cryptophytes, and (d) prymnesiophytes in Marguerite Bay for the 2000-2001 scenario.

Figure 46. The model’s annual cycles of biomass (mg chl $a$ m$^{-3}$) of (a) total chlorophyll, (b) diatoms, (c) cryptophytes, and (d) prymnesiophytes in Marguerite Bay for the 2001-2002 scenario.

Figure 47. Simulated net primary production (g C m$^{-2}$ d$^{-1}$) and grazing losses (g C m$^{-2}$ d$^{-1}$) of (a) diatoms, (b) cryptophytes, and (c) prymnesiophytes in Marguerite Bay during 2000-2001.

Figure 48. Simulated net primary production (g C m$^{-2}$ d$^{-1}$) and grazing losses (g C m$^{-2}$ d$^{-1}$) of (a) diatoms, (b) cryptophytes, and (c) prymnesiophytes in Marguerite Bay during 2001-2002.
Figure 49. (a) The model response of prymnesiophyte biomass (mg chl a m\(^{-3}\)) to perturbation of prymnesiophyte fraction of growth excreted as DOC\(_1\), ψ.  

Figure 50. The model’s Marguerite Bay annual cycles of (a) dissolved organic carbon (DOC\(_1\)+DOC\(_2\)) (μM) and (b) bacterial biomass (mg C m\(^{-3}\)) for 2000-2001 model scenario and (c) total labile dissolved organic carbon (DOC) (μM) and (d) bacterial biomass (mg C m\(^{-3}\)) for 2001-2002 model scenario.  

Figure 51. The simulated time series of ammonium production by zooplankton, microzooplankton, and bacteria (mmol NH\(_4\) m\(^{-2}\) d\(^{-1}\)) in Marguerite Bay for (a) 2000-2001 and (b) 2001-2002 scenarios.  

Figure 52. Simulated annual cycles of ammonium (μM) for (a) case 1 with 2000-2001 physical conditions (Table 8a) and 2001-2002 grazing stress (Table 11b) and (b) case 2 with 2001-2002 physical conditions (Table 8b) and 2000-2001 grazing stress (Table 11a).  

Figure 53. Case 3: simulated annual cycles of (a) bacteria (mg C m\(^{-3}\)), (b) ammonium (μM), (c) total chlorophyll (mg chl a m\(^{-3}\)), and (d) sum of monomeric DOC\(_1\) and macromolecular DOC\(_2\) (μM) for the 2000-2001 scenario with maximal bacteria growth rate of 0.16 d\(^{-1}\).  

Figure 54. Case 4: simulated annual cycles of (a) bacteria (mg C m\(^{-3}\)), (b) ammonium (μM), (c) total chlorophyll (mg chl a m\(^{-3}\)), and (d) sum of monomeric DOC\(_1\) and macromolecular DOC\(_2\) (μM) for the 2001-2002 scenario with maximal bacteria growth rate of 0.16 d\(^{-1}\).  

Figure 55. Simulated time series of total water column nitrification (mmol NH\(_4\) m\(^{-2}\) d\(^{-1}\)) for the 2000-2001 and 2001-2002 scenarios in Marguerite Bay.  

Figure 56. Simulated annual cycles of (a) cryptophyte biomass (mg chl a m\(^{-3}\)), (b) prymnesiophyte biomass (mg chl a m\(^{-3}\)), (c) nitrate concentration (μM), (d) ammonium concentration (μM), (e) DOC\(_1\)+DOC\(_2\) (μM), and (f) bacteria (mg C m\(^{-3}\)) for the 2000-2001 scenario with maximal diatom growth rate μ=0.35 d\(^{-1}\).  

Figure 57. Simulated annual cycles of (a) cryptophyte biomass (mg chl a m\(^{-3}\)), (b) prymnesiophyte biomass (mg chl a m\(^{-3}\)), (c) nitrate concentration (μM), (d) ammonium concentration (μM), (e) DOC\(_1\)+DOC\(_2\) (μM), and (f) bacteria (mg C m\(^{-3}\)) for the 2001-2002 scenario with maximal diatom growth rate μ=0.35 d\(^{-1}\).
Figure 58. Simulated annual cycles of (a) total chlorophyll $a$ biomass (mg chl $a$ m$^{-3}$), (b) nitrate concentration ($\mu$M), (c) ammonium concentration ($\mu$M), (d) DOC$_1$+DOC$_2$ ($\mu$M), and (e) bacteria (mg C m$^{-3}$) for the 2001-2002 scenario with maximal diatom growth rate $\mu=1.05$ d$^{-1}$.

Figure 59. Simulated annual cycles of (a) total chlorophyll biomass (mg chl $a$ m$^{-3}$), (b) nitrate concentration ($\mu$M), (c) ammonium concentration ($\mu$M), (d) DOC$_1$+DOC$_2$ ($\mu$M), and (e) bacteria (mg C m$^{-3}$) for the 2001-2002 scenario with maximal diatom growth rate $\mu=1.05$ d$^{-1}$.

Figure 60. Simulated annual cycles of (a) bacteria (mg C m$^{-3}$), (b) DOC$_1$+DOC$_2$ ($\mu$M), (c) ammonium concentration ($\mu$M), (d) nitrate concentration ($\mu$M), and (e) total chlorophyll biomass (mg chl $a$ m$^{-3}$) for the 2000-2001 scenario with maximal bacteria growth rate $\mu=0.48$ d$^{-1}$.

Figure 61. Simulated annual cycles of (a) bacteria (mg C m$^{-3}$), (b) DOC$_1$+DOC$_2$ ($\mu$M), (c) ammonium concentration ($\mu$M), (d) nitrate concentration ($\mu$M), and (e) total chlorophyll biomass (mg chl $a$ m$^{-3}$) for the 20010-2002 scenario with maximal bacteria growth rate $\mu=0.48$ d$^{-1}$.
Ammonium Distribution and Dynamics in Relation to Biological Production and 
Physical Environment in the Marguerite Bay Region of the West Antarctic 
Peninsula

Yulia Serebrennikova

ABSTRACT

In this study, biogeochemical regimes of Marguerite Bay and the adjacent part of the West Antarctic Peninsula (WAP) continental shelf were delineated through integration of nutrient, hydrographic, and biological measurements obtained during the LTER and SO GLOBEC studies during austral summer, autumn, and winter of 2001 and 2002. 

Marguerite Bay biogeochemical regime was found to differ from those of the adjacent WAP continental shelf. In terms of Treguer and Jacques (1992), Marguerite Bay is a combination of Coastal Continental Shelf Zone (CCSZ) and Seasonal Ice Zone (SIZ) distinguished by shallow mixing regime, high primary production and export production. At the end of the growing season (autumn) in both years, waters in Marguerite Bay were strongly depleted in nutrients (the deficits of total inorganic nitrogen (NO$_3^-$+NO$_2^-$+NH$_4^+$) and silica were >0.6 mol m$^{-2}$ and >2.5 mol m$^{-2}$, respectively). Observed $\Delta$N/$\Delta$P removal ratios of 10-12.5, lower than that of Redfield et al. (1963), and $\Delta$Si/$\Delta$N removal ratios as high as 4-5 indicated the dominance of diatoms. High autumnal ammonium stocks (>0.25 mol m$^{-2}$) were observed in Marguerite Bay and were co-located with the areas of the
highest nutrient deficits suggesting spatial coupling between primary and heterotrophic production during both years. Consistency of this feature was not disrupted by significant interannual variability of biological production in Marguerite Bay that resulted in \( \sim 30-50\% \) reduction in nutrient deficits and ammonium stocks from the first year to the next.

The other two biogeochemical regimes were at the central part of the continental shelf characterized by mixed phytoplankton community and at the outer shelf dominated by diatoms. Both regimes were characterized by considerably lower depletion of nutrients compare to those of the Marguerite Bay regime and were consistent between the two years.

Interannual variability of biological production and possible sources of high ammonium stocks in Marguerite Bay were studied with a one-dimensional model, a modification of that of Walsh et al. (2001). The model attributed the decline in nutrient deficits to the difference in sea ice cover dynamics between two years. The greater sea ice presence led to the somewhat lower primary production during the second year compare to the fist one. Moreover, model’s tight coupling between primary and bacterial production resulted in a decline of bacterial ammonification between the two years. Bacteria were found to be the primary source of ammonium in the Marguerite Bay model. Yet, 3-4-fold fluctuations in macro- and mesozooplankton biomass might have led to 15-25% variability in model’s autumnal ammonium stocks.
1. Introduction

1.1. Ammonium in the Ocean

The study of nitrogen dynamics is important for understanding the structure and functioning of any ecosystem in the ocean, as nitrogen is an essential element for all organisms to grow. In the Southern Ocean, the supply of inorganic nitrogen, mainly in the form of nitrate, is high and rarely growth limiting, except under bloom conditions (Holm-Hansen et al., 1989; Karl et al., 1992). As most of the Southern Ocean is a region of low primary production (Treguer and Jacques, 1992), the macronutrient pool is rarely depleted and Antarctic surface waters stay rich in nitrate and other inorganic macronutrients—phosphate and silicic acid—throughout the growing season. Yet another form of inorganic nitrogen—ammonium—is often present in high concentrations in Antarctic waters. For example, ammonium concentrations up to 4 μM were found in the Ross Sea (Gordon et al., 2000) and 4-10 μM ammonium concentrations are common in the coastal areas west of the Antarctic Peninsula (Koike et al., 1986; Huntley et al., 1987; Owens et al., 1991; Clarke and Leakey, 1996; Serebrennikova and Fanning, 2004). Such high ammonium concentrations make the Antarctic Peninsula a preferred site to study ammonium dynamics in the Southern Ocean.

Ammonium in most of the ocean is principally a surface-water phenomenon; ammonium concentrations are largely undetectable by conventional methods in deep waters. In tropical and subtropical oligotrophic oceanic regions, which account for more than half of the world ocean area, primary production is low and nutrient-limited, and
therefore rapid utilization of ammonium by phytoplankton is invoked to explain the fact that ammonium levels are frequently very low in those regions. Since those areas are characterized by poor seasonality in primary production, utilization of ammonium results in ammonium levels that rarely exceed 0.1 μM (Eppley, 1973; Brzezinski, 1988; Lipschultz et al., 1996; Metzler et al., 1997; Woodward et al., 1999). Yet even in Antarctic waters, where primary production is restricted to a short period of the polar summer due to pronounced seasonal variability in the incoming solar radiation, to low temperatures and to the formation and melting of sea ice (Smith et al., 1996), the nitrate pool is rarely depleted and ammonium appears to be an important and often the major nitrogenous source for Antarctic phytoplankton at some stages of the development of phytoplankton communities (Koike et al., 1986; Goeyens et al., 1998; Sambrotto et al., 2000; Bode et al., 2002). In coastal areas west of Antarctic Peninsula, the levels of nitrate could be reduced to near analytical zero (Holm-Hansen et al., 1989; Dore et al., 1992), and recycling of the ammonium pool could in fact be crucial for maintaining high primary production rates.

It is not clear what the principal sources of ammonium in Antarctic waters are. Ammonium is a major nitrogenous waste excreted by zooplankton (Biggs, 1982; Alcaraz et al., 1998). However, Biggs (1982) and Huntley and Nordhausen (1995) showed that ammonium excretion by larger zooplankton, except exceptionally dense krill swarms, makes a rather small contribution to the ammonium pool. It has been suggested that the largest part of ammonium production in the Antarctic waters should be attributed to the smaller organisms: protozoa and bacteria (Glibert, 1982; Koike et al., 1986; Goeyens et al., 1991; Tupas et al., 1994; Karl et al., 1996). For example, Tupas et al. (1994) found
that 27-55% of the total ammonium in the surface waters near the Antarctic Peninsula is
regenerated by bacteria. Microbial activity may be of predominant importance for
Antarctic remineralization processes. There is evidence that about 50-90 % of the net
primary production in Antarctic waters could be assimilated in the microbial food web,
which is composed of bacterioplankton, heteroflagellates, and protozoa (Lancelot et al.,
1991). However, only a few studies of microbial activity in Antarctic waters have been
done (Burkill et al., 1996).

The fate of ammonium during the Antarctic winter is not fully understood.
Seasonal studies show a decrease in ammonium concentrations from autumn to winter
(Gordon et al., 2000; Serebrennikova and Fanning, 2004). A variety of possible processes
could be responsible, including uptake by phytoplankton and bacteria, ammonium
oxidation, and diffusive mixing with surrounding low-ammonium waters. The first,
primary production, is generally negligible in autumn and winter because of low light
levels in the Southern Ocean.

In the absence of ammonium uptake by primary producers, nitrification--
bacterially mediated chemoautotrophic oxidation of ammonium to nitrite and then to
nitrate-- might be important. Given the low light levels at high latitude and the relatively
low half-saturation constant for ammonium oxidizing bacteria (<1 µM; Olson, 1981)
Antarctic waters appear to be a suitable environment for ammonium-oxidizing bacteria.
However, few studies on nitrification have been conducted in the Southern Ocean. The
ones that have been done give controversial results. They were conducted in different
seasons and locations, making comparison between them difficult. Nitrification rates
were found to be low, and often too low to detect, in the coastal areas of the Southern
Ocean during austral spring and summer (Olson, 1981; Priscu et al., 1990). On other hand, Bianchi et al. (1997) found that the autumnal nitrification rates of 20-30 nM d⁻¹ in the surface waters of the Southern Ocean north to 52°S to be approximately the same order of magnitude as those measured in the nitracline at the temperate latitudes. In addition, Bianchi et al. reported that, at low temperatures, nitrifiers must enhance energy metabolism by oxidizing more substrate; therefore the rates of ammonium oxidation by nitrifiers can be high in winter. However, Dore et al. (1993) found nitrification rates of less than a few nM per day in the waters along the west coast of the Antarctic Peninsula during the austral winter, in agreement with the results of Olson (1981) and Priscu et al. (1990). At these low rates, nitrification may not be a major sink for ammonium in the Antarctic coastal waters.

In the case of the west Antarctic Peninsula, a model study shows that vertical mixing can return nitrate concentrations in the mixed layer depleted during the summer to the high early spring levels during the winter (Klinck et al., 2002). Similarly, the decline in the ammonium concentrations might be to a large degree due to vertical mixing, as ammonium concentrations are generally undetectable in subpycnocline waters.

Ammonium dynamics could also be studied because of its implications in the recycling versus export of organic matter. An important component of studying Antarctic ammonium recycling is to quantify the nutrient depletions, or net community production (NCP), which is a measure of the net production of autotrophs minus the respiration of the entire community (Sweeney et al., 2000a). NCP may be calculated in two ways. One is based on the deficit of CO₂ in the surface layer corrected for the processes unrelated to photosynthesis and respiration. The other is based on the seasonal depletion of nutrients
converted to carbon by employing carbon-to-nutrient ratios. The second approach is advantageous as it avoids the problems associated with ascertaining air-sea gas exchange, which complicates the use of dissolved inorganic carbon (DIC) budgets to estimate NCP (Hoppema and Goeyens, 1999). The NCP approach estimates biological production integrated over the whole growing season whereas the estimates based on in-situ measurements of primary production may under- or over-estimate the seasonal production due to high spatial and temporal variability of biological processes (Moline and Prezlin, 1996; Smith et al., 1996). As most of the organic-matter export occurs in summer and a low amount of organic matter is left in the surface layer in autumn at the end of the growing season (Karl et al., 1996; Sweeney et al., 2000b), estimates of the autumnal nutrient (usually total inorganic nitrogen) deficit might provide a proxy for the seasonal export production. Ammonium standing stocks, in turn, might give estimates of organic matter regenerated in the surface layer.

Regeneration of ammonium in the surface waters has important biogeochemical consequences. The greater the proportion of organic matter that is remineralized in the surface layer of the water column, the lower the proportion of organic matter that is exported into the deep ocean. Assessment of the efficiency of regenerative processes is of a particular importance in the most productive areas of the Southern Ocean, which account for a significant part of net primary production in the Southern Ocean (Treguer and Jacques, 1992). Estimates of the net community drawdown of nutrients, nutrient removal ratios, and nutrient regeneration are useful in differentiating regional biogeochemical regimes. An understanding of the coupling between biogeochemical regimes and the surrounding environment will lead to the prediction of biological
responses to changes in that environment, and is thereby of great importance for understanding the nutrient and carbon cycles in the Southern Ocean.

Given the ecological importance of ammonium, the focus of this research was an examination of the role of ammonium in biological processes and biogeochemical cycles in the Antarctic waters at one of the productive sites of the Southern Ocean, Marguerite Bay, and the adjacent continental shelf west of the Antarctic Peninsula (Fig. 1).

There are three major goals in this dissertation.

The first goal (Chapter 2) is delineation of the mesoscale biogeochemical regimes and nutrient cycling in the study region on the basis of the variability in nutrient distribution and the correlation between nutrient distribution and physical properties of the environment, such as temperature, salinity, and regional circulation. The result should be an understanding of the structure and functioning of the system.

The second goal (Chapter 3) is evaluation of a number of questions that would lead to understanding the ammonium dynamics in the system. These questions relate the causes of the accumulation of the high ammonium pool, the nature of ammonium temporal dynamics (particularly in winter) and the importance of the regenerative processes in the system.

The third goal (Chapter 4) is to construct a numerical model of ammonium dynamics in the system that incorporates the parameterizations derived from the current knowledge of the processes in Marguerite Bay and the other areas of the Southern Ocean.
Fig. 1. Map of Marguerite Bay (MB) and the adjacent WAP continental shelf. The symbols indicate the locations of CTD stations sampled during (a) January of 2001 (LTER), (b) April-May of 2001 (GLOBEC I), (c) July-August of 2001 (GLOBEC II), (d) September of 2001 (LTER), (e) January of 2002 (LTER), (f) April-May of 2002 (GLOBEC III), and (g) August-September of 2002 (GLOBEC IV). The bottom bathymetry contour inside Marguerite Bay indicates the 500-m depth. Bathymetry contour interval = 500m. M.Tr. designates Marguerite Trough. Key to island names: Ad. I. - Adelaide Island, Alex. I. - Alexander Island, C. I. - Charcot Island.

Continued on the next page
Fig. 1 (continued).

Continued on the next page

8
Fig. 1 (continued).
1.2. General characteristics of the area

The study area covered Marguerite Bay (MB) and the adjacent continental shelf west of Antarctic Peninsula, between 65.5 and 70 °S from north of the northern tip of Adelaide Island to Charcot Island (Fig. 1). The West Antarctic Peninsula (WAP) continental shelf is relatively deep (400-600 m) and approximately 200 km wide and has a rugged bottom topography, which is believed to be important in the circulation (Klinck et al., 2004). The region is a highly dynamic coastal continental shelf zone that is directly exposed to the prevailing westerly atmospheric and eastward oceanic circulations and is annually swept by the advance and retreat of seasonal sea ice. Sea ice dynamics largely control the biological production on the WAP continental shelf (Stammerjohn and Smith, 1996).

The water mass structure of the WAP continental shelf consists of Antarctic Surface Water (AASW), which occupies the upper 100-150 m and is replaced by Winter Water (WW) in autumn and winter, and the underlying modified form of Upper Circumpolar Deep Water (UCDW). The modified UCDW (MUCDW) results from mixing of UCDW and AASW (Smith et al., 1999). UCDW and Lower Circumpolar Deep Water (LCDW) are the largest water masses in the Antarctic Circumpolar Current (ACC), which flows northeastward along the WAP shelf break. Warm UCDW (>1.6 °C) and cooler MUCDW (1 °C – 1.6 °C) are rich in nitrate (>33 μM) and phosphate (>2.3 μM). LCDW is rich in silica (>100 μM) and is characterized by salinity maxima (>34.72). The proximity of the ACC to the WAP continental shelf produces on-shelf bottom intrusions of Circumpolar Deep Water associated with the variability of the shelf break topography, the most prominent of which is the Marguerite Trough. This channel
starts near the shelf break northwest of Adelaide Island and runs southeastward into
Marguerite Bay (M. Tr. in Fig. 1 (b, c, f); Smith et al., 1999; Klinck et al., 2004;
Beardsley et al., 2004). ACC forced intrusions of UCDW onto the shelf might then
upwell or mix into the upper water column (Prézelin et al., 2004).

In contrast to most of the Southern Ocean, the waters on the WAP continental
shelf are known to support a significant phytoplankton biomass (Holm-Hansen and
Mitchell, 1991; Smith et al., 1996; Moline and Prezelin, 1996; Prezelin et al., 2000;
Garibotti et al., 2003a; Garibotti et al., 2003b; Garibotti et al., 2005) and large
zooplankton population (Ross et al., 1996; Ross et al., 1998; Lascara et al., 1999; Quentin
and Ross, 2003). The WAP continental shelf is believed to be a spawning site for
Antarctic krill Euphausia superba, which migrate northward during the spring and
summer (Ashjian et al., 2004). The largest phytoplankton blooms usually occur near the
coast. Nearshore conditions—such as water column stabilization due to ice melt, low
wind stress, and, possibly, micronutrient availability—appear to be more favorable in
producing the large phytoplankton blooms (Moline and Prézelin, 1996; Smith et al.,
1998). Non-seasonal episodic diatom dominated blooms may occur at the mid and outer
shelf when ACC-forced intrusions of UCDW upwell into the upper water column
(Prézelin et al., 2000; Prézelin et al., 2004). However, the shelf blooms seem to have
lower magnitude than those inshore (Prézelin et al., 2004; Garibotti et al., 2005).

1.3. Field sampling design and schedule

The results of seven surveys in the area are examined in this study. Four surveys
were conducted in 2001 and three were conducted in 2002 covering summer (January),
autumn (April-May), and winter (July-August-September) seasons in each year (Table 1).
In January of 2001 and 2002, data were collected during the Palmer Long-Term Ecological Research (LTER) program surveys. The sampling locations were located inside Marguerite Bay and along the across-shelf LTER lines 200, 300, and 400 that covered a part of the study area seaward of Adelaide Island with 20-km spacing between the individual stations and 100-km spacing between the lines (Fig. 1a, e). The 2001 and 2002 autumnal and mid-winter data were collected as a part of the US Southern Ocean Global Ocean Ecosystems Dynamics (SO GLOBEC) study (Table 1). The basic SO GLOBEC grid consisted of 13 across-shelf GLOBEC transects with 40-km along-shelf spacing and 10-40 km spacing between individual stations. The total number of stations occupied during each survey varied from 50 to 96 (Table 1, Fig. 1b, c, f, g). Fewer stations were occupied on mid-winter surveys (July-August of 2001 and August-September of 2002) (Fig. 1c, g) than on autumnal surveys (April-May of 2001 and April-May of 2002) (Fig. 1b, f). Also, 15 stations were sampled during a LTER survey conducted from the middle September to the middle of October of 2001 (Table 1, Fig. 1d).

Nutrient analysis for data collected during SO GLOBEC program is given in Serebrennikova and Fanning (2004). Nutrient data from the LTER surveys were provided by M. Vernet (the data are published on LTER web site http://pal.lternet.edu/). In addition to nutrient data I supplemented my study with data on water column hydrography, circulation, primary production, pigment concentration, bacteria and zooplankton abundance and biomass collected by other research groups during the GLOBEC and LTER programs (http://globec.whoi.edu/jg/dir/globec/soglobec/ and http://pal.lternet.edu/).
Table 1. A compilation of SO LTER and GLOBEC survey designations, dates, and stations for the 2001 and 2002 field seasons.

<table>
<thead>
<tr>
<th>Survey</th>
<th>Dates</th>
<th># stations occupied</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTER 01Jan</td>
<td>January 15 – January 24, 2001</td>
<td>30</td>
</tr>
<tr>
<td>GLOBEC I</td>
<td>April 29- June 2, 2001</td>
<td>84</td>
</tr>
<tr>
<td>GLOBEC II</td>
<td>July 27- August 25, 2001</td>
<td>64</td>
</tr>
<tr>
<td>LTER 01Sep</td>
<td>September 14 – October 16, 2001</td>
<td>15</td>
</tr>
<tr>
<td>LTER 02Jan</td>
<td>January 15 – January 24, 2002</td>
<td>31</td>
</tr>
<tr>
<td>GLOBEC III</td>
<td>April 13- May 12, 2002</td>
<td>96</td>
</tr>
<tr>
<td>GLOBEC IV</td>
<td>August 5- September 10, 2002</td>
<td>50</td>
</tr>
</tbody>
</table>
2. Biogeochemical Regimes

2.1. Introduction

The primary focus of this chapter was to assess Net community production (NCP) and biogeochemical regimes for Marguerite Bay and the adjacent area of the WAP continental shelf. NCP, as an imbalance between the autotrophic production and community respiration, provides an estimate of biological production that is representative of the whole growing season. In other words, it accounts for organic matter both accumulated within and exported from the seasonal mixed-layer. Furthermore, at the end of the growing season, when the amounts of both particulate and dissolved organic matter are negligible (Sweeney et al., 2000b), it provides an estimate of the annual export production. In this study, NCP was estimated for the period of spring-to-mid-summer and spring-to-autumn of 2000-2001 and 2001-2002 austral years by quantifying the seasonal nutrient depletion and then converted to carbon removal by employing a C/N ratio based on Redfield et al. (1963). Assessment of phytoplankton NCP, phytoplankton community structure and associated physical environment of the Marguerite Bay area allowed differentiation of the biogeochemical regimes and provided a key to understanding factors controlling biological production in the study area.

In addition to mid-summer and autumn, estimates of nutrient deficits were made for winter observations to complete the evaluation of the seasonal evolution of nutrients in the Marguerite Bay area.

2.2. Hydrographic and physicochemical properties in 2001 and 2002

In January of 2001, the physicochemical properties showed considerable spatial variability throughout the area. Since mixed-layer depth was determined as the depth at
which a change of $\sigma_i$ was $>0.05$ over 5 m interval (Garibotti et al., 2003b), it decreased from offshore to inshore being $<15$ m inside Marguerite Bay (Fig. 2d). Average mixed-layer temperature was the highest inside Marguerite Bay and inshore north of Adelaide Island ($>2^\circ$C) and the lowest at mid-shelf ($<1^\circ$C) (Fig. 2a). Average mixed-layer salinity exhibited an opposite trend with the lowest salinity ($<33$) found inshore in two regions (I- north of Adelaide Island and II- Marguerite Bay) and the highest salinity ($>33.8$) found offshore (Fig. 2b).

Vertical water column stability for the upper mixed-layer (E) was calculated as $E=d\sigma_i/dz *1/\sigma_{i(\text{avg})}$, where $d\sigma_i/dz$ is the vertical gradient of density and $\sigma_{i(\text{avg})}$ is the average density (Garibotti et al., 2003b). In January of 2001, vertical water column stability ranged from 0.3 to $1.8*10^{-3}$ m$^{-1}$ (Table 2). The stability increased from offshore to inshore being the highest ($>1.5*10^{-3}$ m$^{-1}$) inside Marguerite Bay (Fig. 2c). The stability of this shallow mixed-layer was supported by a steep density gradient that resulted most likely from fresh water input from sea ice melting.

In April-May of 2001, average mixed-layer temperatures were generally $<0$ $^\circ$C throughout the study area decreasing from north to south (Fig. 3a). Enhanced annual vertical mixing resulted in a decrease in mixed-layer stability (from $0.93\pm0.45*10^{-3}$ m$^{-1}$ in January to $0.35\pm0.12*10^{-3}$ m$^{-1}$) and deepened the upper mixed-layer (table 2, figures 3c, d). The average mixed-layer salinity during April-May than during January 2001 inside Marguerite Bay (compare Figs. 2b and 3b). Yet, the inshore salinity was still lower than that offshore.

In July-August of 2001, the study area was already ice-covered. The average mixed-layer temperature was near freezing point ($-1.8^\circ$C) throughout the study area (Fig.
Fig. 2. Distribution of physicochemical properties in January of 2001. (a) Average mixed-layer temperature (°C); (b) Average mixed-layer salinity (psu); (c) Vertical stability ($10^{-3}$ m$^{-1}$); (d) Mixed-layer depth (m).

Continued on the next page
Table 2. Averages and ranges for the vertical stability of the mixed layer and mixed layer depth for summer, autumn and winter time surveys in 2001 and 2002. Uncertainties represent one standard deviation for all stations occupied on each survey.

<table>
<thead>
<tr>
<th></th>
<th>Vertical stability (10^{-3} m^{-1})</th>
<th>Mixed-layer depth (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>January 2001</td>
<td>0.93±0.45 [0.30 – 1.80]</td>
<td>32±14 [10 – 82]</td>
</tr>
<tr>
<td>April-May 2001</td>
<td>0.35±0.12 [0.14 – 0.90]</td>
<td>73±23 [30 – 150]</td>
</tr>
<tr>
<td>July-August 2001</td>
<td>0.19±0.07 [0.08 – 0.39]</td>
<td>104±27 [50 – 200]</td>
</tr>
<tr>
<td>September-October 2001</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>January 2002</td>
<td>0.40±0.25 [0.12 – 1.23]</td>
<td>38±16 [8 – 69]</td>
</tr>
<tr>
<td>April-May 2002</td>
<td>0.40±0.15 [0.15 – 0.99]</td>
<td>70±21 [20 – 125]</td>
</tr>
<tr>
<td>August-September 2002</td>
<td>0.16±0.07 [0.01 – 0.34]</td>
<td>110±31 [50 – 200]</td>
</tr>
</tbody>
</table>
Fig. 3. Distribution of physicochemical properties in April-May of 2001. (a) Average mixed-layer temperature (°C); (b) Average mixed-layer salinity (psu); (c) Vertical stability (10⁻³ m⁻¹); (d) Mixed-layer depth (m).

Continued on the next page

20
4a). Sea ice formation resulted in an increase in mixed-layer salinity (Fig. 4b) through brine rejection, a decrease in vertical stability of the upper water column (Table 2, Fig. 4c), and an increase in mixed-layer depth (Table 2, Fig. 4d).

In January 2002, the distribution of physicochemical properties showed some differences from that in January 2001. First, average mixed-layer temperature was approximately 1°C lower in the inshore areas in January 2002 than in January 2001 (compare Figs. 2a and 5a). Second, vertical water column stability decreased between two years (Table 2). Yet, the stability was still the highest inside Marguerite Bay (> 0.8*10^{-3} m^{-1}) (Fig. 5c). The average mixed-layer salinity was <33 inside Marguerite Bay and > 33.8 over the rest of the area sampled during LTER in January 2002 (Fig. 5b). As in January 2001, the mixed-layer depth was the lowest, < 15 m, inside Marguerite Bay in January 2002 (Fig. 5d).

In April-May of 2002, average mixed-layer temperature showed north-south trend with temperature being > -1°C in the northern part of the study area and decreasing to -1.8°C in the southeastern part (Fig. 6a). It should be noted that the southeastern part of the study area was partly ice-covered through summer to autumn. Average mixed-layer salinity showed offshore/inshore trend with the lowest salinity (<33.2) being inside Marguerite Bay (Fig. 6b). The mixed-layer stability was <0.6*10^{-3} m^{-1} throughout most of the study area and >0.8*10^{-3} m^{-1} in the southeastern part of Marguerite Bay (Fig. 6c). In April-May of 2002, average mixed-layer depth was greater than that in January of 2002 and was not statistically different from that in April-May of 2001 (Table 2). In August-September of 2002, physicochemical properties were the same as in July-August of 2001 (Table 2, Fig. 7).
Fig. 4. Distribution of physicochemical properties in July-August of 2001. (a) Average mixed-layer temperature (°C); (b) Average mixed-layer salinity (psu); (c) Vertical stability (10^-3 m⁻³); (d) Mixed-layer depth (m).

Continued on the next page
Fig. 4. (continued).
Fig. 5. Distribution of physicochemical properties in January of 2002. (a) Average mixed-layer temperature (°C); (b) Average mixed-layer salinity (psu); (c) Vertical stability (10⁻³ m⁻¹); (d) Mixed-layer depth (m).

Continued on the next page
Fig. 5. (continued).
Fig. 6. Distribution of physicochemical properties in April-May of 2002. (a) Average mixed-layer temperature (°C); (b) Average mixed-layer salinity (psu); (c) Vertical stability (10⁻³ m⁻¹); (d) Mixed-layer depth (m).

Continued on the next page
To sum up, the inshore mixed-layer of the Marguerite Bay area were less saline and, hence, more stable that that of the offshore waters. This feature was consistent between the two years. The progression from summer to autumn and to winter followed the same pattern in two years, including cooling of the surface waters, deepening of the mixed-layer, and declining water column stability. Yet, the inshore regions of the study area, in particular Marguerite Bay, were significantly colder during the second year than in the first one.

A prominent hydrographic feature observed throughout most of the study area during summer and autumnal surveys in both 2001 and 2002 was the layer of remnant WW formed in the preceding winters. The layer was found between 50 and 150 m deep and was characterized by a minimum in temperature. In January of 2001, temperature in the remnant WW layer ranged from -1°C to -1.8°C with the highest values observed inside Marguerite Bay (Fig. 8a). Distribution of the average mixed-layer temperature also shows the highest values inside Marguerite Bay (Fig. 2a) suggesting that Marguerite Bay WW layer was heated by the warm waters from above the layer. In April-May of 2001, remnant WW temperature ranged from 0°C to -1.6°C with the lowest values found offshore and the highest values found inshore (Fig. 8b).

In January of 2002, the range in temperature of the remnant WW layer was the same as in January of 2001; however, the temperature distribution was different (Fig. 8c). As in January of 2001, it followed the distribution of average mixed-layer temperature, which was the highest in the northern part of study area in January of 2002 (Fig. 5a). As in January of 2002, the highest WW temperatures (> -0.8°C) were found in the northern
Fig. 7. Distribution of physicochemical properties in August-September of 2002. (a) Average mixed-layer temperature (°C); (b) Average mixed-layer salinity (psu); (c) Vertical stability (10^{-3} m^{-1}); (d) Mixed-layer depth (m).

Continued on the next page
Fig. 7. (continued).
Fig. 8. Temperature (°C) distribution at temperature minimum level in (a) January of 2001, (b) April-May of 2001, (c) January of 2002, and (d) April-May of 2002.
Fig. 8. (continued).
part of the study area and the lowest values (<-1°C) were observed in the southern part in April-May of 2002 (Fig. 8d). As mentioned above, the fact that the southern part of the study area was partly ice-covered through summer to autumn might explain this difference in the distribution patterns of WW temperature between two years. The remnant WW layer disappeared by the times of the mid-winter surveys.

The distribution of the temperature maximum below 200 m allows tracking the movement of UCDW onto the WAP continental shelf as the isotherm patterns can be used to approximate the current flow (Klinck et al., 2004). The major concern here is the 1.6°C isotherm that denotes the southern boundary of the ACC and the boundary between UCDW and MUCDW (Smith et al., 1999; Klinck et al., 2004). Fig. 9a-c show that 1.6 °C isotherm was situated along the shelf break in 2001. It extended onto the shelf only in the northern part of the study area and in the central part on transects 7 and 9 indicating onshelf movement of UCDW at these locations (Figs. 9a-c). The intrusion of UCDW onto the shelf identified by 1.6 °C isotherm was associated with a meander in the ACC aligned with northeastern side of Marguerite Trough in the northern part of the study area (Figs. 9a-c). The onshelf intrusion of UCDW in the central part of the study area was associated with a shelf break curvature (Klinck et al., 2004). It was suggested by Prézelin et al. (2004) that the intrusions of UCDW onto the shelf might result in its upwelling into the upper water column. However, it contradicts the observations of remnant WW layer, which was characterized by a minimum in temperature. If the upwelling of warm (>1.6°C) UCDW into the surface waters had occurred between spring and autumn the temperature minimum should have disappeared. Fig. 8a, b show the temperature values at the temperature minimum level being lower than those from above (Figs. 2a and 3a) and
Fig. 9. Distribution of potential temperature (°C) maximum below 200 m in (a) January of 2001, (b) April-May of 2001, (c) July-August of 2001, (d) January of 2002, (e) April-May of 2002, and (f) August-September of 2002.

Continued on the next page
Fig. 9 (continued).
those of UCDW from below indicating no UCDW upwelling along the shelf break in
summer and autumn of 2001. However, there is a possibility that UCDW upwelling had
occurred at the location of the shelf break curvature by August-September of 2001. This
is suggested by the highest mixed-layer salinity and the lowest water column stability
observed at that site in August-September of 2001 (Figs. 4b, c).

In 2002, the 1.6°C isotherm extended somewhat greater inshore than in 2001 from
the shelf break indicating that the ACC actually flowed over the shelf break (Figs. 9d-f).
In January and April-May of 2002, distinct subsurface temperature minima were
observed at the offshore locations. Temperature values at the depths of temperature
minimum (Figs. 8c and d) were lower than those in the surface mixed-layer (Figs. 5a and
6a) and those from below the pycnocline (Figs. 9d and e). Thus, despite the presence of
UCDW at the outer shelf no UCDW upwelling seems to have occurred between summer
and autumn of 2002. Interestingly, the same features (high mixed-layer salinity and low
water column stability) were observed in August-September of 2002 at the location of the
shelf break curvature characterized by on-shelf ACC fluctuations (Fig. 9f) as in July-

In both years a meander of the ACC onto the shelf in the northern part of the
study area produced an offshore to inshore flow, which was compensated by inshore to
offshore flow in the central part of the study area thus forming a mesoscale cyclonic gyre
between the coast of Adelaide Island and the shelf break (Klinck et al., 2004).

A seasonal buoyancy-forced coastal current associated with the low salinity
coastal waters resulting from spring and summer ice melt was observed along the west
coast of Adelaide Island in the autumns and winters of 2001 and 2002 (Klinck et al.,
2004). This current was most likely a continuation of the nearshore south-southwestern flow to the north of the study area observed during the previous studies on the WAP continental shelf (Smith et al., 1999; Klinck et al., 2004). The current entered Marguerite Bay and formed a gyre inside the bay and then extended from the bay southwestward along the west coast of Alexander Island (Beardsley et al., 2004). Overall, the south-southwestern flow dominated in the study area in the autumns and winters of 2001 and 2002 (Klinck et al., 2004). However, the flow was somewhat weaker during the mid-winter surveys than during the autumnal surveys.

2.3. Nutrient deficit calculations

Estimates of nutrient deficits during the periods of biological activity (i.e., spring for January data and spring-autumn for April-May data) were calculated using the method of Rubin et al. (1998) and Ishii et al (2002). The deficit calculations were based on vertically integrated depletions of nutrients in the surface layer down to the depths of a layer of remnant WW, which was distinguished by a subsurface temperature minimum as illustrated in Fig. 10 and salinity around 34 (not shown) during 2001 and 2002 summer LTER and autumnal SO GLOBEC surveys. Since this layer forms at the end of the winter every year, its properties, which are still present in the summer and autumn, are reasonable approximations of the entire mixed-layer in the late winter and early spring (Ishii et al., 2002). For example, the shaded profile in Fig. 10a shows approximated early spring concentrations of total inorganic nitrogen (TIN) for a station inside Marguerite Bay. Thus, WW layer nutrient concentrations can be considered the starting values before the subsequent spring and summer primary production and nutrient uptake occur. Vertically integrated reductions in nutrient concentrations below those in the underlying
remnant WW layer indicate the magnitudes of the nutrient deficits produced during the growing seasons.

This method of calculating nutrient deficits assumes that the changes of nutrient concentrations within the WW layer from spring to autumn were negligible. Possible causes, if any, for such changes would be photosynthesis and/or remineralization of organic matter within the WW layer, vertical and lateral mixing, and dilution by ice melt water. Mixing and dilution by ice-melt can affect the overlying mixed layer as well.

Fig.10. Illustration of the deficit calculation technique on example of TIN deficit calculation at a station inside Marguerite Bay. (a) Vertical profiles of total inorganic nitrogen (TIN) (µM) during January, May, and August of 2001. The shaded portion of the graph was believed to correspond to the late winter (or early spring) conditions of TIN in the study area. The range in the shaded values presented was from actual TIN measurements within WW layer for the entire study area (mean ± 2S.D., n=114; Table 3) during January 2001 and April-May 2001 and was believed to reflect the TIN content of pre-bloom conditions. Thus, for each season TIN deficit at this station was the depth-integrated difference between the season’s TIN vertical profile and shaded portion of the graph. (b) Corresponding vertical profiles of temperature (°C).
Table 3. The remnant WW layer properties in the study region including the average depth of the layer (mean ±2S.D.), the range in silica concentration and the values (mean ±2S.D.) of salinity, phosphate, and total inorganic nitrogen (TIN=[NO$_3$]$_{-}$+[NO$_2$]$_{-}$+[NH$_4$]) observed in the layer in summers and autumns of 2001 and 2002.

<table>
<thead>
<tr>
<th>Study</th>
<th>WW layer depth, m</th>
<th>Salinity</th>
<th>Silica range, μM</th>
<th>Phosphate, μM</th>
<th>TIN, μM</th>
</tr>
</thead>
<tbody>
<tr>
<td>January, 2001</td>
<td>80 ± 35</td>
<td>34.0 ±0.1</td>
<td>42-83</td>
<td>2.02 ± 0.06</td>
<td>31.6 ± 1.0</td>
</tr>
<tr>
<td>April-May, 2001</td>
<td>100 ± 40</td>
<td>34.0 ±0.1</td>
<td>55.5 – 95.2</td>
<td>2.16 ± 0.04</td>
<td>31.1 ± 0.8</td>
</tr>
<tr>
<td>January, 2002</td>
<td>76 ± 40</td>
<td>34.0±0.2</td>
<td>52-86</td>
<td>2.16 ± 0.07</td>
<td>30.5 ± 1.0</td>
</tr>
<tr>
<td>April-May, 2002</td>
<td>85 ± 50</td>
<td>33.9 ± 0.3</td>
<td>60.0 - 96.0</td>
<td>2.18 ± 0.6</td>
<td>30.8 ± 1.0</td>
</tr>
</tbody>
</table>

There are few data on biological activity (photosynthesis, remineralization) in the WW layer, but it was not considered to be important because of a comparison between the properties of the WW layer in April-May of 2001 with the same properties of the WW layer earlier in the year. LTER data in the study region showed that salinities (34.0±0.1), nitrate concentrations (31.6±0.8 μM), and phosphate concentrations (2.08±0.04 μM) in the WW layer in January 2001 (Vernet, 2001), when it had temperatures ranging from -1°C to -1.8°C (average -1.6°C±0.2°C, Fig. 8a), were not statistically different from those observed in this layer in the following autumn three months later, during April-May of 2001 (Table 3). This suggests that the remnant WW layer present in the April-May of 2001 had not undergone any significant changes in its salinity or other chemical properties during the growing season. In April-May of 2002 the remnant WW layer had been similarly unchanged since January of 2002 (Table 3).

The temperature of the remnant WW layer ranged from 0°C to -1.6°C (average – 0.9°C ± 0.5°C, Fig. 8b, d) during April-May of 2001 and April-May of 2002. The fact
that this temperature range is larger and slightly more positive than the “typical” WW
temperature range of -1.0°C to -1.8°C (Hofmann et al., 1996) suggests that the layer may
have been eroded by mixing with warmer deep water from below and/or warmer near-
surface waters from above between the January and April-May surveys in 2001 and 2002.
Since nutrient concentrations increase with depth, mixing with waters from below the
WW layer would tend to increase the nutrient concentrations within the layer, while
mixing with the waters from above would tend to decrease them. However the potential
impact on nutrient concentrations in either the WW or the overlying mixed layer is
difficult to ascertain. The overall net effect, if any, of this vertical mixing of nutrients
from below the WW layer into the surface mixed layer would probably be to cause the
nutrient deficit estimates to be too low, i.e., minima. There are insufficient data to predict
the error in those estimates that might result, but, because of the above-mentioned
agreement between the January WW layer data and April-May WW layer data (Table 3),
it can be assumed it to be slight. Inshore areas of the WAP continental shelf are more
productive and therefore more nutrient-depleted than offshore areas (Moline and
Prézélin, 1996; Smith et al., 1998; Prézélin et al., 2000; Garibotti et al., 2003a; Garibotti
et al., 2003b). Lateral transport of offshore waters inshore might also be expected to lead
to an underestimation of the actual inshore nutrient deficits. It will be shown later in the
nutrient deficit distribution section that nutrient deficit isopleths were nearly parallel to
the coast. Thus, alongshore lateral transport should have led to negligible changes in
nutrient deficits as it would have brought in waters with approximately the same nutrient
deficit values.
The evidence that could be found indicate that the nutrient deficit calculations were not significantly affected by mixing or variations in WW nutrient concentrations during the WAP growing season. The impact of dilution of mixed-layer nutrient concentrations by melt water was also minimal. When those nutrient concentrations were scaled to a constant salinity of 34.0, nutrient deficits changed by about 2%.

Estimates of nutrient deficits for the mid-winter surveys were done differently. In July-August of 2001, September-October of 2001, and August-September of 2002, WW from the preceding winters could not be identified as it had completely gone and new WW started to form (Klinck et al., 2004). However, nutrient concentrations during these surveys had not yet reached the values of the previous winter (Fig. 10a). Thus, nutrient deficits were integrated from the surface down to the level, where nutrient concentrations fell within the ranges of those approximated for the early spring (shaded area in Fig. 10a). These early spring nutrient concentrations were constructed from those observed in the remnant WW layer during the summers and autumns of 2001 and 2002 (Table 3).

Nutrient deficit calculations were made for TIN ([NO$_3^-$] + [NO$_2^-$] + [NH$_4^+$]), silica, and phosphate for all stations within the study area (Table 1).

The error of the calculation of the nutrient deficit estimates was computed by multiplying the average WW layer depth by twice the standard deviation of the WW layer values for total inorganic nitrogen (TIN) and phosphate, which are summarized in Table 3. For silica, the error was computed by considering the closest sampling locations as the replicates. The resulting errors are ±0.2 mol m$^{-2}$ for silica, ±0.08 mol m$^{-2}$ for TIN, and ±0.004 mol m$^{-2}$ for phosphate.
2.4. Nutrient deficits in 2001 and 2002

2.4.1 Nutrient deficits in January of 2001

In January of 2001, the \( \text{Def} \) (TIN) ranged from 0.26 to 0.85 mol m\(^{-2} \) in the part of the study area sampled during the LTER program (Table 4). The \( \text{Def} \) (TIN) distribution showed an offshore/inshore trend with the highest deficit values (>0.6 mol m\(^{-2} \)) found in two nearshore areas—north of Adelaide Island and around the southern tip of Adelaide Island, at the entrance to Marguerite Bay (Fig. 11a). Those were the same areas where the lowest mixed-layer salinity and the highest mixed-layer stability were observed (Figs. 2b, c). \( \text{Def} \) (PO\(_4\)) ranged from 0.02 to 0.07 mol m\(^{-2} \) (Table 4) and its distribution followed that of \( \text{Def} \) (TIN) (Fig. 12a). \( \text{Def} \) (SIL) ranged from 0.2 to 1.8 mol m\(^{-2} \) (Table 4). The \( \text{Def} \) (SIL) distribution followed that of \( \text{Def} \) (TIN) as well—the \( \text{Def} \) (SIL) was <0.5 mol/m\(^{2} \) at the offshore locations and >1.0 mol m\(^{-2} \) inshore where the highest \( \text{Def} \) (TIN) was observed (Fig. 11b).

Given the coherence between nutrient deficit distributions described above, the regressions between deficits showed linearity (\( r^2 = 0.85, 0.71, \) and 0.68 for the \( \text{Def} \) (TIN) – \( \text{Def} \) (PO\(_4\)), \( \text{Def} \) (SIL) – \( \text{Def} \) (TIN), and \( \text{Def} \) (SIL) – \( \text{Def} \) (PO\(_4\)) regressions, respectively, Fig. 12). The individual \( \text{Def} \) (TIN) to \( \text{Def} \) (PO\(_4\)) ratios (9.4–14.9, average 12.2±1.6) observed in January of 2001 were lower than the classical Redfield \( \Delta N/\Delta P \) ratio of 16.

The most likely reason for the low \( \Delta N/\Delta P \) ratio was presented in Sweeney et al. (2000a) who reported \( \Delta N/\Delta P \) utilization ratios of 10.0±0.7 for diatoms opposite to \textit{Phaeocystis sp.} that showed \( \Delta N/\Delta P \) utilization ratios of 18.6±0.4 in the Ross Sea. This suggests the dominance of diatoms in nutrient utilization in the Marguerite Bay region in January of 2001. Fig. 11c shows that the highest \( \Delta N/\Delta P \) ratios (>14) were observed at the
Table 4. Averages and ranges for the deficits of total inorganic nitrogen (\textit{Def} (TIN)), phosphate (\textit{Def} (PO\textsubscript{4})), silica (\textit{Def} (SIL)) and Net community production (NCP) estimates integrated to the depths of the remnant WW layer for summer, autumn, and winter time surveys in 2001 and 2002.

Uncertainties represent one standard deviation for all stations occupied on each survey. All units are in mol m\textsuperscript{-2}.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{Def} (TIN)</td>
<td>0.50 ±0.2</td>
<td>0.54 ±0.2</td>
<td>0.2 ±0.2</td>
<td>0.17 ±0.06</td>
<td>0.56 ±0.2</td>
<td>0.4 ±0.3</td>
<td>0.07 ±0.1</td>
</tr>
<tr>
<td>\textit{Def} (TIN) range</td>
<td>0.26 – 0.85</td>
<td>0.1 – 1.37</td>
<td>0.01 – 0.5</td>
<td>0.02 – 0.25</td>
<td>0.23 – 1.0</td>
<td>0.09 – 0.9</td>
<td>0.0 – 0.2</td>
</tr>
<tr>
<td>\textit{Def} (PO\textsubscript{4})</td>
<td>0.04 ±0.01</td>
<td>0.04±0.02</td>
<td>0.02±0.02</td>
<td>0.013 ±0.004</td>
<td>0.04±0.02</td>
<td>0.04±0.02</td>
<td>0.007 ±0.01</td>
</tr>
<tr>
<td>\textit{Def} (PO\textsubscript{4}) range</td>
<td>0.02 – 0.07</td>
<td>0.01 – 0.12</td>
<td>0.0 – 0.04</td>
<td>0.002 – 0.02</td>
<td>0.02 – 0.08</td>
<td>0.01 – 0.09</td>
<td>0.0 – 0.02</td>
</tr>
<tr>
<td>\textit{Def} (SIL)</td>
<td>0.7 ±0.4</td>
<td>2.0±1.0</td>
<td>0.9±1.0</td>
<td>0.5±0.2</td>
<td>0.9±0.4</td>
<td>1.6±1.3</td>
<td>0.3 ±0.5</td>
</tr>
<tr>
<td>\textit{Def} (SIL) range</td>
<td>0.2 – 1.8</td>
<td>1.0 – 5.4</td>
<td>0.03 – 2.4</td>
<td>0.1 – 0.7</td>
<td>0.3 – 1.8</td>
<td>0.6 – 4.2</td>
<td>0.0 – 0.9</td>
</tr>
<tr>
<td>NCP</td>
<td>3.5 ±1.2</td>
<td>3.8 ±1.9</td>
<td>--</td>
<td>--</td>
<td>3.9 ±3.2</td>
<td>2.8 ±2.3</td>
<td>--</td>
</tr>
<tr>
<td>NCP range</td>
<td>1.8 – 6.0</td>
<td>0.7 – 9.6</td>
<td>--</td>
<td>--</td>
<td>1.4 – 7.1</td>
<td>0.2 – 6.3</td>
<td>--</td>
</tr>
</tbody>
</table>
Fig. 11. (a) Distribution of $\Delta$P (TIN), mol m$^{-2}$, (b) $\Delta$P (SIL), mol m$^{-2}$, (c) $\Delta$N/$\Delta$P ratio, and (d) $\Delta$Si/$\Delta$N ratio in January of 2001.

Continued on the next page
Fig. 11. (continued).
Fig. 12. (a) The relationships between Def(TIN) and Def(PO₄) for January of 2001. R² = 0.85, n = 28, Def(TIN) = 11.02 (±0.9)* Def(PO₄) + 0.04 (±0.04). (b) The relationships between Def(SIL) and Def(TIN) for January of 2001. R² = 0.71, n = 28, Def(SIL) = 2.0 (±0.2)* Def(TIN) - 0.2 (±0.1). (c) The relationships between Def(SIL) and Def(PO₄) for January of 2001. R² = 0.68, n = 28, Def(SIL) = 23.7 (±3.2)* Def(PO₄) - 0.2 (±0.1). All units are in mol m⁻².
central part of the sampled area, and the lowest ratios (< 12) were found offshore during January of 2001. The relative dominance of diatoms is supported by high $\Delta$Si/$\Delta$N ratios (1.4±0.5) found in the region (Fig. 11d) as diatoms use large quantities of silica to form their opal tests. In January 2001, the $\Delta$Si/$\Delta$N utilization ratios ranged from 0.5 on LTER line 300 to 2.1 inside Marguerite Bay, but most of the study area had $\Delta$Si/$\Delta$N ratios >1 (Fig. 11d). Generally, $\Delta$Si/$\Delta$N equal 1 is chosen as a limit indicative the dominance of diatoms.

Another way to assess the phytoplankton community structure is by using accessory carotenoid pigments. The carotenoids alloxanthin, 19'-hexanoyloxy-fucoxanthin (HEX), 19'-butanoyloxy-fucoxanthin (BUT), and fucoxanthin are used as specific biomarkers indicative of cryptophytes, prymnesiophytes, pelagophytes, and diatoms, respectively (Bidigare et al., 1996; Prézelin et al., 2000; DiTullio and Smith, 1996; Garibotti et al., 2003a). Although some pigments may also occur as secondary pigments in other algal groups, the impact of sharing of pigments between groups is negligible (Prézelin et al., 2000; Garibotti et al., 2003a). Fig. 13 shows fucoxanthin being the most abundant pigment in January of 2001 (Vernet, 2001). Because its amount relative to total pigment in diatom cells is relatively small (Bidigare et al., 1996) the dominance of diatoms can be indicated by fucoxanthin being 30% or greater of the total accessory pigments (Sweeney et al., 2000b). In January of 2001, the relative abundance of fucoxanthin was >32% supporting the results of $\Delta$N/$\Delta$P and $\Delta$Si/$\Delta$N ratio analysis. HEX, which is indicative of prymnesiophytes, was abundant at the mid-shelf locations of lines 200 and 300, in the middle of the gyre, indicating a mixed phytoplankton community at those locations.
2.4.2. Nutrient deficits in April-May of 2001

In April-May of 2001, Def (TIN) and Def (SIL) exhibited strong offshore/inshore trends. The lowest values (<0.2 mol m\(^{-2}\) and < 1.5 mol m\(^{-2}\), respectively) were near the shelf break and the largest values (>1 mol m\(^{-2}\) and > 3.5 mol m\(^{-2}\), respectively) were found inside Marguerite Bay and between Alexander and Charcot Islands (Figs. 14a, b). Corresponding Def (PO\(_4\)) values were <0.02 mol m\(^{-2}\) offshore and > 0.7 mol m\(^{-2}\) inshore.

Comparing the nutrient deficits observed in January and April-May of 2001 in a part of the study area next to Adelaide Island the following was found. Def (TIN) did not change significantly (Figs. 11a and 14a) however, a considerable increase in Def (SIL) was observed, especially near the southern tip of Adelaide Island where the Def (SIL) values increased from 1.5 to 3.5 mol m\(^{-2}\) (compare Figs. 11b and 14b). An interesting pattern of along-shore variability in the distribution of the nutrient deficits in April-May of 2001 was also found. Five peaks of high nutrient deficit values were identified (A1-E1 in Figs. 14a, b). A1 and B1 were located along the Adelaide Island coast; the largest one, C1, was inside Marguerite Bay; and D1 and E1 were found near Alexander and Charcot Islands south of MB. Interestingly, peaks A1 and B1 in April-May were found at the locations where high nutrient deficits peaks were identified in January (Fig. 11a, b).

Regressions between deficits showed linearity for April-May of 2001, especially the Def (TIN) – Def (PO\(_4\)) regression (\(r^2>0.9\), Fig. 15a). The \(r^2\) for Def (SiO\(_2\)) – Def (TIN) and Def (SiO\(_2\)) – Def (PO\(_4\)) were 0.76 and 0.88, respectively (Fig. 15b, c). Thus, the net consumption of TIN, silica and PO\(_4\) appears to have been well correlated. Averages of the ratios of the individual Def (TIN) and corresponding Def (PO\(_4\)) provide measures of the net N: P incorporation ratios during the 2001 growing season that can be compared to the
Fig. 13. Distribution of pigments averaged over the euphotic zone in January of 2001. (a) fucoxanthin as a marker for diatoms, (b) 19'-hexanoyloxy-fucoxanthin (HEX) as a marker for prymnesiophytes, (c) 19'-butanoyloxy-fucoxanthin (BUT) as a marker for pelagophytes, and (d) alloxanthin as a marker for cryptophytes. All units are in mg m⁻³.

Continued on the next page
Fig. 13. (continued).
Fig. 14. (a) Distribution of Def (TIN), mol m$^{-2}$, (b) Def (SIL), mol m$^{-2}$, (c) $\Delta$N/$\Delta$P ratio, and (d) $\Delta$Si/$\Delta$N ratio in April-May of 2001. Regions of high deficits are indicated by letters A1-E1.

Continued on the next page
Fig. 14. (continued).
Fig. 15. (a) The relationships between Def (TIN) and Def (PO₄) for April-May of 2001. R²=0.94, n=65, Def (TIN) =11.6 (±0.8)* Def (PO₄) + 0.03 (±0.04). (b) The relationships between Def (SIL) and Def (TIN) for April-May of 2001. R²=0.76, n=65, Def (SIL) =3.3 (±0.5)* Def (TIN) + 0.2 (±0.3). (c) The relationships between Def (SIL) and Def (PO₄) for April-May of 2001. R²=0.88, n=65, Def (SIL) =42.8 (±2.0)* Def (PO₄) + 0.1 (±0.1). All units are in mol m⁻².
classical Redfield $\Delta N/\Delta P$ ratio of 16. Similarly to January of 2001, those averages in April-May ($12.4 \pm 1.7$) were definitely lower than Redfield $\Delta N/\Delta P$ ratio of 16. As mentioned, the low $\Delta N/\Delta P$ utilization ratios indicate the dominance of diatoms (Sweeney et al., 2000a; Arrigo et al., 1999). Thus, the low $\Delta N/\Delta P$ utilization ratios found in the Marguerite Bay region in April-May of 2001 most likely indicate a dominance of diatoms during the preceding growing season. Averages of individual ratios of $Def$ (SIL) to $Def$ (TIN) were $3.9 \pm 1.2$ and for April-May of 2001, indicative of the dominance of diatoms.

The distributions of $\Delta N/\Delta P$ and $\Delta Si/\Delta N$ ratios in April-May of 2001 was somewhat different from those in January of 2001. In April-May, the lowest $\Delta N/\Delta P$ ratios ($< 12$) were observed inside Marguerite Bay (Fig. 14c) where the $\Delta N/\Delta P$ ratios were approximately 13 in January (Fig. 11c). The decrease in the Marguerite Bay $\Delta N/\Delta P$ ratios was accompanied by an increase in the Marguerite Bay $\Delta Si/\Delta N$ ratio from 2.1 to 4.5 from January to April-May (Figs. 11d and 14d). Seaward of Adelaide Island $\Delta Si/\Delta N$ ratio also increased from the average of 1.4 in January to the average of 4 in April-May but $\Delta N/\Delta P$ ratios were approximately the same – they averaged 12 in January and in April-May. This indicates a persistent importance of diatoms during the 2001 growing season. The highest $\Delta N/\Delta P$ (>14) and the lowest $\Delta Si/\Delta N$ (<2.5) ratios were observed in the southwestern portion of the study region in April-May of 2001 (Figs. 14c, d). To sum up, the inshore regions of high nutrient deficits showed only low $\Delta N/\Delta P$ and high $\Delta Si/\Delta N$ values whereas the offshore regions of low nutrient deficits exhibited both high-end and low-end values for $\Delta N/\Delta P$ and $\Delta Si/\Delta N$ ratios.
2.4.3. *Nutrient deficit in July-August of 2001*

In July-August of 2001, average nutrient deficits were approximately 50% lower than those in April-May of 2001 (Table 4). In general, the trends in the distribution of Def (TIN) and Def (SIL) in July-August were similar to those in April-May with the largest values (>0.3 mol m$^{-2}$ and >1 mol m$^{-2}$, respectively) observed inshore and the lowest values (<0.2 mol m$^{-2}$ and <0.75 mol m$^{-2}$, respectively) found seaward (Figs. 16a, b). Figs. 16a, b show that the peaks of high nutrient deficits were still present inside Marguerite Bay and between Charcot and Alexander Islands (B2 and C2), the same locations were elevated nutrient deficit values were found in April-May (C1 and E1 in Figs. 14a, b). There were no peaks of elevated nutrient deficits along the Adelaide Island coast in July-August (A2 in Figs. 16a, b). In fact, the nutrient deficits were among of the lowest of the whole study region (Def (TIN) <0.05 mol m$^{-2}$ and Def (SIL) <0.25 mol m$^{-2}$) at that location (Figs. 16a, b). The vertical sections of temperature, salinity, and nitrate distributions along the transect 2 in July-August show isolines sloping upward near the coast of Adelaide Island indicating an upwelling (Fig. 17). This upwelling was likely to deliver high-nutrient waters to the surface near the west coast of Adelaide Island bringing nutrient concentrations in the surface waters close to the early spring values and thus nutrient deficits to zero. Also, the lowest values of Def (TIN) (<0.1 mol m$^{-2}$) and Def (SIL) (<0.5 mol m$^{-2}$) were found in the offshore southwestern part of the study area, characterized by the curvature of shelf break (Fig. 16a, b). Since this region was characterized by the lowest water column stability (<0.12*10$^{-3}$ m$^{-1}$) in the study region (Fig. 4c), it is possible that these lowest deficits were caused by UCDW upwelling.
Fig. 16. (a) Distribution of $Def$ (TIN), mol m$^{-2}$, and (b) $Def$ (SIL), mol m$^{-2}$, in July-August of 2001. Regions of low (A2) and high (B2, C2) deficits are indicated.
Fig. 17. Vertical sections of the distribution of (a) potential density and (b) nitrate concentration (μM) along transect #2 (see Fig. 1c for the location) in July-August of 2001. Zero distance denotes the location of the most seaward station of the sections.

Similarly to April-May of 2001, Def (TIN), Def (PO₄), and Def (SIL) appeared to have been well correlated (r² were 0.96, 0.78, and 0.70 for the Def (TIN) – Def (PO₄), Def (SIL) – Def (TIN), and Def (SIL) – Def (PO₄) regressions, respectively, Fig. 18) in July-August of 2001.

2.4.4. Nutrient deficit in September-October of 2001

In September-October of 2001, as a part of LTER program 15 stations were sampled near the mouth of Marguerite Bay (Fig. 1d). These stations were sampled approximately a month later since the entrance to Marguerite Bay was studied during GLOBEC II survey and allow investigating the changes in nutrient concentrations as winter progressed. The
Fig. 18. (a) The relationships between Def (TIN) and Def (PO₄) for July-August of 2001. R²=0.96, n=69, Def (TIN) = 12.5 (±0.3)* Def (PO₄) + -0.01 (±0.01). (b) The relationships between Def (SIL) and Def (TIN) for July-August of 2001. R²=0.79, n=69, Def (SIL) = 3.8 (±0.2)* Def (TIN) + 0.05 (±0.06). (c) The relationships between Def (SIL) and Def (PO₄) for July-August of 2001. R²=0.77, n=69, Def (SIL) = 48.5 (±3.0)* Def (PO₄) + 0.0 (±0.01). All units are in mol m⁻².
average $Def$ (TIN) and $Def$ (SIL) were 0.20 mol m$^{-2}$ and 0.9 mol m$^{-2}$, respectively, at the mouth of Marguerite Bay in July-August of 2001 (Fig. 16a, b). By mid-September, the deficits decreased to 0.17 mol m$^{-2}$ and 0.5 mol m$^{-2}$, respectively, amounting to ~15-40% of the August deficit values (Table 4, Fig. 19a, b).

2.4.5. Nutrient deficit in January of 2002

In January of 2002, the distribution of $Def$ (TIN) exhibited features similar to those in January 2001. The highest $Def$ (TIN) values (> 0.7 mol m$^{-2}$) were found inshore in two regions -- near the northern and southern tips of Adelaide Island, and the lowest values (<0.4 mol m$^{-2}$) were observed at the offshore locations (Fig. 20a). The $Def$ (PO$_4$) followed $Def$ (TIN) (Fig. 21a): the highest $Def$ (PO$_4$) values (>0.06 mol m$^{-2}$) were found inshore and the lowest values (<0.03 mol m$^{-2}$) were found offshore. The highest $Def$ (SIL) (>1.2 mol m$^{-2}$) were found at the entrance to Marguerite Bay and at mid-shelf north of Adelaide Island, the lowest $Def$ (SIL) (<0.6 mol m$^{-2}$) were observed on line 300 and at the offshore locations of line 200 (Fig. 20b, see Fig. 1e for the station locations).

The nutrient deficits were less correlated in January of 2002 than in January of 2001. The $r^2$ values were 0.84, 0.52, and 0.67 for $Def$ (TIN) – $Def$ (PO$_4$), $Def$ (SiO$_2$) – $Def$ (TIN), and $Def$ (SiO$_2$) – $Def$ (PO$_4$) regressions, respectively (Fig. 21). A wider range of individual $\Delta N/\Delta P$ ratios (8.4 – 17.6) was observed in January of 2002 than in January of 2001. High $\Delta N/\Delta P$ ratios (>15 in Fig. 20c) were found at the middle of line 200 and at the inshore locations of line 300. The $\Delta N/\Delta P$ ratios <12 were found offshore and at the entrance to Marguerite Bay (Fig. 20c). As mentioned, low $\Delta N/\Delta P$ ratios can be attributed to the dominance of diatoms and high $\Delta N/\Delta P$ ratios may be an indicative of prynnesiophytes (Sweeney et al., 2000a). This was consistent with the distribution of
Fig. 19. (a) Distribution of $Def$ (TIN), mol m$^{-2}$, and (b) $Def$ (SIL), mol m$^{-2}$, in September-October of 2001.
Fig. 20. (a) Distribution of $D_{ef}$ (TIN), mol m$^{-2}$, (b) $D_{ef}$ (SIL), mol m$^{-2}$, (c) $\Delta N/\Delta P$ ratio, and (d) $\Delta Si/\Delta N$ ratio in January of 2002.

Continued on the next page
ΔSi/ΔN ratios – the high ΔSi/ΔN values (>1) were co-located with low ΔN/ΔP values and the lowest ΔSi/ΔN values (<1) were co-located with the highest ΔN/ΔP values (Fig. 20d). ΔSi/ΔN ratio was >1.5 at the entrance to Marguerite Bay (Fig. 20d).

2.4.6. Nutrient deficit in April-May of 2002

In April-May of 2002, the distributions of the deficits were consistent with those in January of 2002 and somewhat different from those in April-May of 2001 (Fig. 22). Although the averages and ranges in the deficits were not significantly different between two autumns (Table 4), the trends in the horizontal distribution of Def (TIN) and Def (SIL) were not strong. The Def (TIN) > 0.6 mol m\(^{-2}\) and Def (SIL) > 2.5 mol m\(^{-2}\) were found in a narrow region between the southern tip of Adelaide Island and the central part of Marguerite Bay (Fig. 22a, b) – approximately the same location where the highest Def (TIN) and Def (SIL) were observed in the preceding summer (Fig. 20a, b). Corresponding Def (PO\(_4\)) were > 0.06 mol m\(^{-2}\). As in 2001, a considerable increase in the Def (SIL) values (from 1.6 mol m\(^{-2}\) to >3 mol m\(^{-2}\) was observed between January and April-May of 2002 (Table 4, compare Figs. 20b and 22b).

As in 2001, regressions between deficits showed more linearity for April-May than for January of 2002, especially the Def (TIN) – Def (PO\(_4\)) regression (r\(^2\)>0.9, Fig. 23). Another similarity between the autumns of 2001 and 2002 was that the average ΔN/ΔP ratios (11.0±1.6), again, were significantly lower than Redfield ΔN/ΔP ratio of 16 and ΔSi/ΔN ratios (average -- 4.1±1.1) were as high as in April-May of 2001. However, the distributions of ΔN/ΔP and ΔSi/ΔN ratios were different between two autumns. In April-May of 2002, the lowest ΔN/ΔP (<12) and the highest ΔSi/ΔN (up to 6) ratios were observed in the southern part of the study area, seaward of Alexander Island (Figs 22c
Fig. 22. (a) Distribution of $\text{Def}$(TIN), mol m$^{-2}$, (b) $\text{Def}$(SIL), mol m$^{-2}$, (c) $\Delta$N/$\Delta$P ratio, and (d) $\Delta$Si/$\Delta$N ratio in April-May of 2002.

Continued on the next page

67
Fig. 22. (continued).
and d) whereas, this region exhibited $\frac{\Delta N}{\Delta P}$ ratios > 14 and $\frac{\Delta Si}{\Delta N}$ < 2.5 in April-May of 2001 (Fig. 14c, d). This suggests a change in phytoplankton community structure between two years at that location. As in April-May of 2001, the region of high TIN and silica deficits showed the low $\frac{\Delta N}{\Delta P}$ and high $\frac{\Delta Si}{\Delta N}$ ratios and there was a wide range of $\frac{\Delta N}{\Delta P}$ and $\frac{\Delta Si}{\Delta N}$ ratios in the regions of low nutrient deficits in April-May of 2002 (Fig. 22).

2.4.7. Nutrient deficit in August-September of 2002

In August-September of 2002, due to the heavy sea ice only a part of the study area was sampled (Fig. 1g). Average nutrient deficit values were lower than those observed in September-October of 2001 (Table 4). Given the uncertainties of the nutrient deficit estimates summarized above, the nutrient deficits were practically zero over the study area except for its southeastern portion (Fig. 24a, b). In the southern part of study area, the 2002 August-September Def (TIN) and Def (SIL) were similar to those in July-August of 2001 (compare Figs. 16a, b and 24a, b). It should be noted that in July-August of 2001 the study area was sampled from north to south, whereas in August-September of 2002 the sampling proceeded from south to north. Thus, the southern part of the study region was sampled at the beginning of August during both mid-winter surveys in 2001 and 2002, whereas the northern part of the study area was sampled in September in 2002, a month later in the season than during the previous mid-winter survey. Def (TIN), Def (PO4), and Def (SIL) again appeared to have been well correlated ($r^2$ were 0.96, 0.78, and 0.71 for the Def (TIN) – Def (PO4), Def (SiO2) – Def (TIN), and Def (SiO2) – Def (PO4) regressions, respectively, Fig. 25).
Fig. 23. (a) The relationships between Def (TIN) and Def (PO4) for April-May of 2002. R^2=0.92, n=88, Def (TIN) =10.8 (±0.7) * Def (PO4) + 0.01(±0.02). (b) The relationships between Def (SIL) and Def (TIN) for April-May of 2002. R^2=0.62, n=88, Def (SIL) =3.3 (±0.6) * Def (TIN) + 0.2 (±0.2). (c) The relationships between Def (SIL) and Def (PO4) for April-May of 2002. R^2=0.76, n=88, Def (SIL) =41.3 (±2.5) * Def (PO4) + 0.05 (±0.1). All units are in mol m$^{-2}$. 
Fig. 24. (a) Distribution of $Def$ (TIN), mol m$^{-2}$, and (b) $Def$ (SIL), mol m$^{-2}$, in August-September of 2002.
Fig. 25. (a) The relationships between Def (TIN) and Def (PO4) for August-September of 2002. $R^2=0.96$, $n=52$, $Def \text{ (TIN)} = 10.7 \pm 0.3 \times Def \text{ (PO4)} + 0.00 \pm 0.00$. (b) The relationships between Def (SIL) and Def (TIN) for August-September of 2002. $R^2=0.78$, $n=52$, $Def \text{ (SiO2)} = 3.8 \pm 0.3 \times Def \text{ (TIN)} + 0.0 \pm 0.0$. (c) The relationships between Def (SIL) and Def (PO4) for August-September of 2002. $R^2=0.71$, $n=52$, $Def \text{ (SiO2)} = 49.3 \pm 3.0 \times Def \text{ (PO4)} + 0.0 \pm 0.0$. All units are in mol m$^{-2}$. 
Fig. 26. Vertical sections of the distribution of (a) potential density (°C) and (b) nitrate concentration (µM) along transect #2 (see Fig. 1g for the location) in August-September of 2002. Zero distance denotes the location of the most seaward station of the sections.

As in July-August of 2001, waters along the west coast of Adelaide Island were characterized by nearly zero nutrient deficits (Def (TIN) <0.05 mol m⁻² and Def (SIL) <0.2 mol m⁻² in Figs. 24a, b). The isolines of density and nitrate on the vertical sections along the transect 2 in August-September of 2002 were rising toward the coast indicating an upwelling (Fig. 26). Also in August-September of 2002, the southwestern part of the study area was characterized by the lowest Def (TIN) (<0.05 mol m⁻²) and Def (SIL) (<0.1 mol m⁻²) and the lowest water column stability (0.1*10⁻³ m⁻¹ in Fig. 7c) that might be related to UCDW upwelling. Both these features seem to be consistent from winter 2001 to winter 2002.

From the calculated nutrient deficits for January and April-May of 2001 and 2002 net community production (NCP) can be estimated. There are some important considerations. First, as mentioned, it was assumed that the changes in the nutrient content in the surface layer above the remnant WW layer since early spring to autumn in both years were largely the results of biological activity, not physical mixing. Second, NCP values are commonly presented as carbon deficits. Thus, it is needed to convert the nutrient deficits by employing a stoichiometric carbon-to-nutrient ratio. The C/P and C/Si ratios have been shown to exhibit a considerable variability depending on the dominant phytoplankton group in the Southern Ocean (Bates et al., 1998; Rubin et al., 1998; Sweeney et al., 2000a). The C/N ratio has been found not to vary significantly and thus seems to be an appropriate ratio to use (Bates et al., 1998; Rubin et al., 1998; Sweeney et al., 2000a). Here a stoichiometric C/N ratio of 7 observed in the Pacific sector of the Southern Ocean is used to convert \( \text{Def} (\text{TIN}) \) to carbon deficits (Rubin et al., 1998).

The NCP values calculated as described above ranged from 1.8 to 6.0 mol m\(^{-2}\) in January of 2001 (Table 4). Based on the distribution of \( \text{Def} (\text{TIN}) \) shown in Fig. 11a, in January of 2001 the highest NCP values (>4.2 mol m\(^{-2}\)) should have been nearshore and located in two regions, north and south of Adelaide Island. The lowest NCP values (<2.8 mol m\(^{-2}\)) should have been offshore. Distribution of the euphotic zone average chlorophyll \( a \) concentration showed a similar pattern with the highest values (>5 mg m\(^{-3}\)) being north and south of Adelaide Island and the lowest values (<1 mg m\(^{-3}\)) offshore (Fig. 27a). This finding is consistent with the results of the previous summer studies on
the WAP shelf that found phytoplankton biomass to be the highest in the inshore areas (Moline and Prézelin, 1996; Smith et al., 1998; Garibotti et al., 2003b). The findings of April-May of 2001 are consistent with those of January of 2001. The NCP values for April-May ranged from 0.7 to 9.6 mol m$^{-2}$ (Table 4). The highest April-May NCP values (>4.2 mol m$^{-2}$) should have been located in one or more of five areas (A1-E1 in Fig. 14a, b), two of which, A1 and B1, were co-located with two high nutrient areas found in January. Primary production was very low in the Marguerite Bay region in April-May of 2001: it was 0.17 mg C m$^{-2}$ d$^{-1}$ in the center of the gyre that occupied the northern part of the study region (Klinck et al., 2004) and coincided with a maximum in chlorophyll $a$ concentration (>1 mg m$^{-3}$ in Fig. 28) and was <0.01 mg C m$^{-2}$ d$^{-1}$ in the rest of the study area (Vernet et al., 2002). These findings indicate the end of the growing season for most of the study region and the depletion of nutrients observed in April-May of 2001 was a result of the primary production that took place before the time of the survey. Although somewhat elevated chlorophyll $a$ concentrations and primary production rates were observed in the gyre, this late bloom was at a stage of the demise (Wiebe et al., 2002a).

As mentioned, NCP values estimated for April-May of 2001 represented net community production for the entire 2000-2001 growing season, while NCP estimates for January of 2001 represented that for a period from the beginning of the growing season, presumably November-December 2000, till January 2001. Yet, NCP values for January and April-May of 2001 were not statistically different (Table 4). Since these NCP estimates were based on the depletions of TIN, this suggests greater regeneration of
Fig. 27. Distribution of (a) average euphotic zone chlorophyll a concentration (mg m\(^{-3}\)) and (b) average euphotic zone phaeopigment concentration (mg m\(^{-3}\)) in January of 2001.
Fig. 28. Distribution of chlorophyll a concentration averaged over the upper 50 m of the water column (mg m$^{-3}$) in April-May of 2001.

nitrogen after January in 2001. Respiration should have had a stronger effect over the whole growing season than in summer.

A combination of several factors supports high production in the nearshore areas. Nearshore phytoplankton are less likely to be carried to depth out of the euphotic zone because of greater stability of the upper water column nearshore as it was found for January of 2001 (Fig. 2c). Melt water from sea and glacial ice enhances the seasonal pycnocline at the base of the mixed-layer, and protection from winds and storms by the continental land mass slows vertical mixing (Moline and Prézelin, 1996; Smith et al., 1998).

In 2002, the picture was somewhat different. In January of 2002, the nutrient deficits and NCP values (1.4 – 7.1 mol m$^{-2}$) were approximately the same as in January of 2001
(Table 4). Also, the highest NCP values should have been located in same two areas as in January of 2001 (compare Figs. 11a and 20a). Interestingly, a peak of high average chlorophyll \( a \) concentration (>10 mg m\(^{-3} \)) was not co-located with the high nutrient deficit region observed at the entrance to Marguerite Bay in January of 2002 (compare Figs. 29a and 20a, b). Average chlorophyll \( a \) concentration was >1.5 mg m\(^{-3} \) north of Adelaide Island and <0.5 mg m\(^{-3} \) over the rest of the study area (Fig. 29a). However, elevated average phaeopigments concentrations (>15 mg m\(^{-3} \)) were co-located with that high nutrient deficit region (compare Figs. 29b and 20a, b). Presence of such high phaeopigments concentrations indicated a recent grazing event as phaeopigment is a result of break down of chlorophyll \( a \) by zooplankton (DiTullio and Smith, 1996). Average phaeopigments concentration was <0.2 mg m\(^{-3} \) over the rest of the study area (Fig. 29b). Thus, overall pigment (chlorophyll \( a \) + phaeopigments) concentration followed nutrient deficit in January of 2002.

In April-May of 2002, the average nutrient deficits and NCP values (2.8±2.3 mol m\(^{-3} \)) were about the same as in April-May of 2001 (3.8±1.9 mol m\(^{-3} \)); however, both the high-end and low-end values in autumn 2002 were lower than those in autumn 2001 (Table 4). The most pronounced decrease in NCP between the two years occurred in the inner part of Marguerite Bay and along the coasts of Alexander and Charcot Islands since NCP is calculated from \( \text{Def (TIN)} \), i.e. compare \( \text{Def (TIN)} \) distributions in Figs. 14a and 22a.

The distribution of the highest \( \text{Def (TIN)} \) went from being in five areas in April-May of 2001 (A1-E1 in Fig. 14a) to essentially only one area near the southern tip of Adelaide Island in April-May of 2002 (Fig. 22a). Interestingly, a decaying autumnal
Fig. 29. Distribution of (a) average euphotic zone chlorophyll $a$ concentration (mg m$^{-3}$) and (b) average euphotic zone phaeopigment concentration (mg m$^{-3}$) in January of 2002.
phytoplankton bloom in the gyre region was observed in April-May of 2002 as in the previous autumn (Wiebe et al., 2002a). The rest of the study area was characterized by low chlorophyll a concentrations (Fig. 30) and negligible primary production rates (Vernet et al., 2002).

A possible explanation for the decrease in the autumnal nutrient drawdown values, and therefore in autumnal NCP values, in 2002 versus 2001 is the difference in environmental conditions, in particular, sea ice cover. In 2000-2001, the Marguerite Bay region was practically ice-free by January 2001 (Fig. 31). In 2001-2002, the sea ice retreat from Marguerite Bay started only in February and Marguerite Bay the southeastern part of the
study region were partly ice-covered through summer into autumn (Fig. 32). There was no significant difference in the magnitude of nutrient drawdown between January of 2001 and January of 2002 (Table 4) as only the northern part of the study area, which was ice-free, was sampled during LTER program in both years. The ice-cover most likely restricted light availability for the water-column phytoplankton and thus, prevented high phytoplankton bloom development in the inner part of Marguerite Bay and between Charcot and Alexander Islands. Those were the areas where the highest nutrient deficits were found in April-May of 2001 (C1 and E1 in Fig. 14a, b). The decrease in the summer-time phytoplankton biomass would have resulted in the lower nutrient deficits observed in those areas in April-May of 2002 (Fig. 22a, b). An influence of sea-ice dynamics on phytoplankton biomass variability has been found in the previous observations on the WAP (Smith et al., 1998).

The Marguerite Bay NCP estimates (and nutrient deficits) can be compared to values obtained in the oligotrophic Pacific sector of the Southern Ocean (Rubin et al., 1998) and the highly productive Ross Sea (Sweeney et al., 2000a, 2000b). Although Sweeney et al. (2000a, b) used different approaches to calculate nutrient deficits (differences between profiles integrated to a depth not necessarily related to the presence of WW) and NCP values (depth-integrated CO₂ drawdown), they had results which could be compared to those of this study. Averaged 2001 and 2002 January deficits and NCP estimates (Table 4) were lower than those of Sweeney et al. (2000a) for the Ross Sea in summer of 1997 (Table 5). The April-May deficits and NCP estimates of 2001 and 2002 (Table 4) were similar to those for the Ross Sea in the autumn of 1997 (Table 5).
Fig. 31. Sea ice extent and concentration (%) in Marguerite Bay (MB) and the adjacent part of the WAP continental shelf for 15th day of each month from November of 2000 to June of 2001 as derived from Special Sensor Microwave Imager (SSM/I) satellite data (Data were courtesy of J. Hyatt (WHOI)). Grey color indicates land.
Fig. 32. Sea ice extent and concentration (%) in Marguerite Bay (MB) and the adjacent part of the WAP continental shelf for 15th day of each month from November of 2001 to June of 2002 as derived from Special Sensor Microwave Imager (SSM/I) satellite data (Data were courtesy of J. Hyatt (WHOI)). Grey color indicates land.
Table 5. Averages and ranges for the deficits of total inorganic nitrogen (TIN), phosphate, silica and Net community production (NCP) estimates from the summer and autumnal 1997 JGOFS survey in the Ross Sea, which are reported in Sweeney et al. (2000b) and from the summer data of the southern Pacific, which are reported in Rubin et al. (1998). All units are in mol m\(^{-2}\).

<table>
<thead>
<tr>
<th></th>
<th>Ross Sea (summer)</th>
<th>Ross Sea (autumn)</th>
<th>Southern Pacific</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIN</td>
<td>1.05 ±0.37</td>
<td>0.46 ±0.17</td>
<td>0.27 ±0.12</td>
</tr>
<tr>
<td>TIN range</td>
<td>--</td>
<td>--</td>
<td>0.13 – 0.45</td>
</tr>
<tr>
<td>PO(_4)</td>
<td>0.06 ±0.02</td>
<td>0.02 ±0.01</td>
<td>0.02 ±0.01</td>
</tr>
<tr>
<td>PO(_4) range</td>
<td>--</td>
<td>--</td>
<td>0.007 – 0.031</td>
</tr>
<tr>
<td>Silica</td>
<td>0.30 ±0.29</td>
<td>0.49 ±0.22</td>
<td>1.14 ±0.73</td>
</tr>
<tr>
<td>Silica range</td>
<td>--</td>
<td>--</td>
<td>0.22 – 1.97</td>
</tr>
<tr>
<td>NCP</td>
<td>7.3±2.2</td>
<td>3.9±0.9</td>
<td>1.7±0.8</td>
</tr>
<tr>
<td>NCP range</td>
<td>4.4 – 10.8</td>
<td>3.0 – 5.5</td>
<td>0.81 – 2.76</td>
</tr>
</tbody>
</table>

However, the Marguerite Bay region is very heterogeneous. Def (TIN) <0.3 mol m\(^{-2}\) and NCP <2 mol m\(^{-2}\) estimates observed beyond the shelf break in the Marguerite Bay region in January and April-May of 2001 and 2002 were rather similar to the NCP values in low-productivity High Nutrient Low Chlorophyll (HNLC) waters of the southern Pacific (0.8 – 2.8 mol m\(^{-2}\) in table 5; Rubin et al., 1998). Def (TIN) >0.9 mol m\(^{-2}\) and NCP >6.3 mol m\(^{-2}\) estimates found in the Marguerite Bay region in January and April-May of 2001 and 2002 were greater than the summernal estimates from the Ross Sea and were closer to the summertime Ross Sea NCP estimates by Sweeney et al. (2000a): 4.4 – 10.8 mol m\(^{-2}\) (Table 5). In those regions of high nutrient deficits phytoplankton
were found to be capable to utilize fully the available nutrients. In fact, TIN and phosphate concentrations in the euphotic zone were \(<0.6 \mu M\) and \(<0.2 \mu M\), respectively, in January of 2001 and \(<7 \mu M\) and \(<0.3 \mu M\), respectively, in January of 2002 inside Marguerite Bay. Those were the conditions at which one of the nutrients — TIN in January of 2001 (TIN/PO\(_4\) <3) and phosphate in January of 2002 (TIN/PO\(_4\) >20) — was limiting phytoplankton growth.

\(\text{Def (SIL)}\) in the Marguerite Bay region in January of 2001 and 2002 (0.7±0.4 mol m\(^{-2}\) and 0.9±0.4 mol m\(^{-2}\)) and in April-May of 2001 and 2002 (2.0±2.0 mol m\(^{-2}\) and 1.6±1.3 mol m\(^{-2}\)) showed a tendency to be larger than those from the Ross Sea in both summer and autumn (0.3±0.29 mol m\(^{-2}\) and 0.49±0.22 mol m\(^{-2}\); Sweeney et al., 2000b), supportive of the greater importance of diatoms and silica utilization in the Marguerite Bay region.

2.6. **Nutrient utilization ratios**

Although there was a substantial degree of linearity between \(\text{Def (TIN)}\), \(\text{Def (PO}_{4}\)), and \(\text{Def (SIL)}\) in January and April-May of 2001 and 2002 (Figs. 12, 15, 21, and 23) that implies a rather uniform structure of phytoplankton communities in the entire study area, individual \(\Delta N/\Delta P\) and \(\Delta Si/\Delta N\) ratio showed wide ranges of values.

Interestingly, the inshore areas that showed NCP values >4.2 mol m\(^{-2}\) also showed low \(\Delta N/\Delta P\) and high \(\Delta Si/\Delta N\) on all four surveys (12.4±1.4 and 1.6±0.4 in January of 2001, 12.0±1.5 and 3.7±0.9 in April-May of 2001, 12.3±1.5 and 1.7±0.4 in January of 2002, and 11.6±1.3 and 3.8±0.9 in April-May of 2002). \(\Delta N/\Delta P\) ratios were consistent between all four surveys (t-test, \(p=0.8\)) and indicate the dominance of diatoms in those areas (Sweeney et al., 2000a). Sweeney et al. (2000a) speculated that the increased
uptake of phosphate relative to nitrogen by diatoms is for luxury storage and that diatoms are likely to change their $\Delta N/\Delta P$ utilization ratio when phosphate becomes limiting. However, the data presented in this study showed the persistence of low $\Delta N/\Delta P$ utilization ratio despite significant depletion of phosphate.

High $\Delta Si/\Delta N$ values observed in the inshore areas are indicators of diatom-domination according to Sweeney et al. (2000a). Assuming $\Delta C: \Delta N =$7 mol mol$^{-1}$ (Rubin et al., 1998) to convert $\Delta Si/\Delta N$ averages to $\Delta Si/\Delta C$, $\Delta Si/\Delta C$ were 0.23±0.06 for January of 2001 and 2002 and 0.56±0.18 and 0.59±0.16 for April-May of 2001 and 2002, respectively, and reflect the average net incorporation ratios of silica to carbon in the WAP plankton during the two growing seasons. These $\Delta Si/\Delta C$ ratios observed in the Marguerite Bay region in both years were considerably higher than those (0.11±0.04) observed in diatom-dominated regions of the Ross Sea by Sweeney et al. (2000a). However, they were consistent with the high values of $\Delta Si/\Delta C = 0.66±0.2$ (Rubin et al., 1998) measured in the Pacific sector of the Southern Ocean and $\Delta Si/\Delta C$ ratios from 0.23 to 0.62 were observed in the southwestern Ross Sea (Smith and Nelson, 1985; Nelson and Smith, 1986; Nelson et al., 1996; Smith et al., 1996). Observations by Takeda et al. (1998) indicate that high $\Delta Si/\Delta C$ ratios in diatoms might be a result of micronutrient (i.e. iron) limitations. However, the observations from the January studies indicate that other factors were likely to limit phytoplankton growth in the inshore regions of the Marguerite Bay area in 2001 and 2002. Given that there was a substantial increase in $\Delta Si/\Delta N$ and $\Delta Si/\Delta C$ ratios between January and April-May of both years, a possible contributing factor to high $\Delta Si/\Delta C$ and $\Delta Si/\Delta N$ ratios for April-May of 2001 and 2002 is de-coupling of silica and nitrogen cycles: soft-tissue nitrogen is more labile than frustule silica.
(DeMasters et al., 1996). Soft-tissue remineralization within the surface mixed-layer, coupled with export of silica frustules from the mixed-layer, could thus help to cause an increase in the net $\Delta$Si/$\Delta$N ratios (Nelson et al., 1996; Ishii et al., 2002).

Although there was a decrease in the maximal nutrient drawdown in April-May of 2002 relative to April-May of 2001 (Table 4), the nutrient utilization ratios ($\Delta$N/$\Delta$P and $\Delta$Si/$\Delta$N) were not significantly different between two autumns (t-test, $p=0.7$ and $p=0.9$, respectively), suggesting a considerable similarity in high biomass phytoplankton community structure between two years. The interannual variability in the magnitude of the phytoplankton bloom (i.e. NCP) apparently had little impact on the composition of phytoplankton population.

In contrast, the areas with low NCP values ($<4.2$ mol m$^{-2}$) showed both high end and low end $\Delta$N/$\Delta$P and $\Delta$Si/$\Delta$N ratios during all four surveys. According to Sweeney et al. (2000a) high $\Delta$N/$\Delta$P and low $\Delta$Si/$\Delta$N ratios should be reflected in a change in the phytoplankton community structure. Indeed, relatively high $\Delta$N/$\Delta$P and low $\Delta$Si/$\Delta$N ratios were found in the gyre region in January of 2001 and 2002 and were co-located with peaks of prymnesiophytes abundance in January of 2001 (Figs. 11c, d and 13b). The pigment data for January of 2002 are not available yet. Local dominance of phytoplankton groups other than diatoms has been reported for the WAP shelf from summer-time studies (Prézelin et al., 2000; Garibotti et al., 2003b; 2005). However, by the end of the growing season this region was represented by diatom-dominated communities in both years (Wiebe et al., 2002a). The low $\Delta$N/$\Delta$P and high $\Delta$Si/$\Delta$N ratios observed in this region in April-May of 2001 and 2002 showed that non-diatomaceous phytoplankton was less important than diatoms over the whole growing season.
The occurrence of low-biomass diatom-dominated phytoplankton assemblages in the northern part of the study area at the offshore locations in January of 2001 and 2002 might have been related to the UCDW bottom intrusions onto the shelf as it was suggested by Prézélin et al. (2004). Figs. 9a and 9d show temperatures >1.6°C occupying approximately the same areas where ΔN/ΔP utilization ratios <12 and ΔSi/ΔN utilization ratios >1 were observed (Figs. 11 and 20). Relatively high ΔSi/ΔN and low ΔN/ΔP ratios in the northern part of the study area were also found in the following autumns (Figs. 14 and 22). However, ΔN/ΔP ratios >16 and ΔSi/ΔN ratios <2 found in the region of the shelf break curvature in April-May of 2001 (Fig. 14c, d)—another site of the UCDW intrusion (Fig. 9b)—suggest that the intrusion had little effect on phytoplankton community structure at that site.

2.7. Seasonal variability in nutrient deficits

The nutrient deficits decreased by approximately 50% on average between April-May of 2001 and July-August of 2001 and by approximately 30% between July-August and September-October of 2001 (Table 4). The decrease in nutrient deficits between April-May of 2002 and August-September of 2002 was greater than that in 2001, approximately 75% on average of the April-May values in 2002 (Table 4). Given the errors of the nutrient deficit calculation summarized on page 37, the nutrient deficit values observed inside Marguerite Bay in September-October of 2001 (Fig. 19) and in the northern part of the study area in September of 2002 (Fig. 24) were close to zero, indicating that the annual nutrient cycle had been nearly complete by the end of the sampling periods in October and September, respectively.
The decrease in the nutrient deficits observed from autumn to winter in both years is a consequence of the enhanced vertical mixing that resulted from cooling of the surface waters and ice formation, when rejected brines increase the mixed-layer salinity and a decrease the mixed-layer stability (Table 2). The vertical mixing deepened the mixed-layer (Table 2) and brought nutrient rich waters to the surface.

Wintertime upwelling during both study years brought nutrient deficits down to zero near the west coast of Adelaide Island (Figs. 16 and 24). Its mechanism is not quite clear. Also there is a controversy: a coastal current that flowed southward along the west coast of Adelaide Island in winter should have actually led to downwelling. A possible explanation for this is that the surface current was weak (Klinck et al., 2004) and should have not affected the deeper layers. However, this current might have played a role in mixing of zero deficit waters from the west of Adelaide Island with the waters inside Marguerite Bay, which still had relatively high nutrient deficit values (Figs. 16, 19 and 24) and were on the path of the current (Klinck et al., 2004). Contours of nutrient deficit distributions in Figs. 16, 19, and 24 suggest protrusion of nearly zero deficit values along the path of the current.

Another site in the study area where the zero nutrient deficits were observed in July-August of 2001 and August-September of 2002 was the curvature of the shelf break seaward of Alexander Island. This site was characterized by the lowest mixed-layer stability that was likely related to the ACC deflections onto the shelf.

2.8. Summary

Seasonal progression of the changes in nutrient deficits that resulted from phytoplankton growth and net community production was examined for the region of
Marguerite Bay in 2001 and 2002. Deficits of total inorganic nitrogen (nitrate + nitrite + ammonium), phosphate, and silica were computed as vertically integrated depletions of these nutrients from surface down to the base of the WW layer, which retained its early spring chemical properties during the growing season. The highest nutrient deficits and NCP values always occurred in the nearshore parts of the Marguerite Bay region. The fact that these observations are consistent with the previous studies on the WAP continental shelf suggests the interannual consistency of the phytoplankton blooms. The study area appeared to be a combination of a HNLC zone occupying middle and outer shelf and highly productive coastal zone where higher nutrient uptake by phytoplankton means nutrients can become factors limiting phytoplankton growth. Despite the fact that the averages of the nutrient deficits and NCP values were not significantly different between 2001 and 2002, the inshore nutrient deficits and NCP values showed a considerable interannual variability that was most likely related to the differences in sea ice dynamics between the two years.

Increased vertical mixing and, possibly, remineralization led to 50-75% decrease in nutrient deficits between autumn and mid-winter in both years. At two locations within the study area vertical mixing was intensified by upwelling of nutrient rich deep waters to the surface.

Net nutrient utilization ratios showed a remarkable consistency between the two years and allow dividing study area into three biogeochemical regimes. The first biogeochemical regime found inshore was characterized by high nutrient removal and low $\Delta N/\Delta P$ and high $\Delta Si/\Delta N$ removal ratios indicative of the dominance of diatoms in summer and autumns of 2001 and 2002. The second biogeochemical regime was situated
at the central part of the gyre that occupied the northern part of the study region. This low-nutrient depletion regime was characterized by mixed phytoplankton community of diatoms and prymnesiophytes and, therefore, had relatively high $\Delta N/\Delta P$ and low $\Delta Si/\Delta N$ removal ratios in summers of 2001 and 2002 and showed a change in phytoplankton community structure toward the dominance of diatoms by the autumns of 2001 and 2002. The third biogeochemical regime was also characterized by low magnitude of nutrient depletions but low $\Delta N/\Delta P$ and high $\Delta Si/\Delta N$ removal ratios indicative of the dominance of diatoms and was observed at the outer shelf. This regime was, possibly, influenced by UCDW intrusions onto the shelf.

The higher $\Delta Si/\Delta N$ removal ratios observed in autumns relative to those in summers in both years that may be a result of preferential remineralization of nitrogen relative to silica in the surface layer during the growing season. Overall, non-diatomaceous phytoplankton groups seemed not important in nutrient utilization in the Marguerite Bay region.
3. Ammonium

3.1. Ammonium stocks distribution in 2001 and 2002

A complete picture of the total ammonium in the system is best achieved by calculating standing ammonium stocks. The procedure is to integrate the ammonium concentration profile at each station from the surface down to the depth of zero ammonium concentration (approximately 200 m).

The usefulness of this approach can be illustrated by an example from the Ross Sea JGOFS Antarctic Environment and Southern Ocean Process Study (AESOPS) summer and autuminal data. Although the highest AESOPS ammonium concentrations were lower in autumn (2.5 µM) than in summer (4 µM), the dispersion of ammonium in the surface mixed layer in autumn caused standing stocks to be higher in autumn (~0.6 mol m⁻²) than in summer (~0.3 mol m⁻²) (data were obtained from Codispoti, 1997). A focus on ammonium concentration exclusively can be misleading.

In January of 2001, LTER found high ammonium concentrations (up to 5 µM) in the study area. Vertical profiles of ammonium typically showed ammonium concentrations to be low at the surface, to increase with depth down to a subsurface ammonium maxima at approximately 40-50 m and then to decrease gradually with depth to zero at approximately 200 m. Fig. 33a illustrates vertical distribution of ammonium concentration on LTER line 200 (see Fig. 1a for the location) in January of 2001. The subsurface peaks of ammonium concentration were distributed randomly along the line not showing any clear pattern (Fig. 33a). The distribution of ammonium concentration along other lines (300 and 400) was similar to that on line 200.
Fig.33. Vertical distribution of ammonium concentration (µM) on (a) line 200 in January of 2001, (b) transect 5 in April-May of 2001, (c) line 200 in January of 2002, and (d) transect 5 in April-May of 2002.

Continued on the next page
Fig. 33 (continued).
Ammonium standing stocks ranged from 0.06 to 0.37 mol m$^{-2}$ (Table 6) and had a patchy distribution pattern. Generally, ammonium stocks were $> 0.2$ mol m$^{-2}$ in the northern part of the study area on line 400 and $< 0.2$ mol m$^{-2}$ on lines 200 and 300 (Fig. 34a). Elevated ammonium stocks ($> 0.25$ mol m$^{-2}$) observed north of Adelaide Island and inside Marguerite Bay (Fig. 34a) coincided with peaks of high $Def$ (TIN) and $Def$ (SIL) values (Fig. 11a, b).

In April-May of 2001, the pattern of vertical distribution of ammonium concentration found on GLOBEC I differed from that found by LTER in January of 2001. Fig. 33b illustrates vertical distribution of ammonium concentration on GLOBEC transect 5 (see Fig. 1b for the location). At nearly every GLOBEC station, ammonium concentrations were the highest and uniformly distributed in the upper 30-100 m of the water column and then rapidly decreased with depth to zero. The highest ammonium concentration was 4.5 μM.

Standing stocks of ammonium ranged from 0.05 to 0.58 mol m$^{-2}$ in April-May of 2001 (Table 6). The highest ammonium stocks ($> 0.45$ mol m$^{-2}$) were found inside Marguerite Bay and near Alexander and Charcot Islands (Fig. 34b). The lowest stocks ($< 0.1$ mol m$^{-2}$) covered the northern and central part of the study area (Fig. 34b). There was approximately 50% decrease in ammonium stocks in the northern part of the study area between January and April-May of 2001 (compare Figs. 34a, b). However, ammonium stocks increased from 0.25 mol m$^{-2}$ to 0.35 mol m$^{-2}$ at the entrance to Marguerite Bay between summer and autumn (Fig. 34a, b). The high ammonium standing stocks found in the Marguerite Bay region are comparable to ammonium stocks
Table 6. Averages and ranges for the ammonium stocks ($\text{NH}_4\text{ST}$) and nitrite stocks ($\text{NO}_2\text{ST}$) for summer, autumn and winter time LTER and GLOBEC surveys to the Marguerite Bay area during 2001 and 2002. Uncertainties represent the standard deviation for all stations occupied on each survey. All units are in mol m\(^{-2}\).

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NH}_4\text{ST}$</td>
<td>0.20 ±0.08</td>
<td>0.22 ±0.14</td>
<td>0.08 ±0.04</td>
<td>0.004±0.007</td>
<td>0.25 ±0.09</td>
<td>0.16 ±0.06</td>
<td>0.04 ±0.02</td>
</tr>
<tr>
<td>$\text{NH}_4\text{ST}$ range</td>
<td>0.06 – 0.37</td>
<td>0.05 – 0.58</td>
<td>0.004 – 0.19</td>
<td>0.00 – 0.03</td>
<td>0.12 – 0.47</td>
<td>0.05 –0.31</td>
<td>0.001 – 0.10</td>
</tr>
<tr>
<td>$\text{NO}_2\text{ST}$</td>
<td>0.037±0.012</td>
<td>0.027±0.01</td>
<td>0.009±0.003</td>
<td>0.004±0.006</td>
<td>0.027±0.008</td>
<td>0.028 ±0.009</td>
<td>0.012 ±0.008</td>
</tr>
<tr>
<td>$\text{NO}_2\text{ST}$ range</td>
<td>0.020 – 0.057</td>
<td>0.012 – 0.06</td>
<td>0.003 – 0.020</td>
<td>0.0 – 0.021</td>
<td>0.012 – 0.050</td>
<td>0.008 – 0.055</td>
<td>0.0 – 0.031</td>
</tr>
</tbody>
</table>
Fig. 34. Distribution of ammonium stocks in (a) January of 2001, (b) April-May of 2001 (Letters A1-E1 indicate the regions of high ammonium stocks); (c) July-August of 2001 (Letters indicate the regions of low (A2) and high (B2 and C2) ammonium stocks), (d) January of 2002; (e) April-May of 2002 (Letters A3-C3 indicate the regions of high ammonium stocks), (f) August-September of 2002. All units are in mol m$^{-2}$.

Continued on the next page
Fig. 34 (continued).

Continued on the next page
Fig. 34 (continued).
of ~0.6 mol m$^2$ calculated for the autumnal Ross Sea JGOFS (AESOPS) data of Codispoti (1997). Interestingly, the locations of the regions of high ammonium stocks (A1-E1 in Fig. 34b) coincided with the locations of the regions of high nutrient deficit (A1-E1 in Fig. 14a, b) observed during April-May of 2001.

In July-August of 2001, ammonium concentrations were <2.2 µM and were uniform throughout the mixed-layer at each station (not shown); ammonium stocks ranged from 0.004 to 0.19 mol m$^{-2}$ (Table 6). Marguerite Bay remained the region of the highest ammonium stocks (>0.15 mol m$^{-2}$), consistent with the ammonium stock distribution in April-May of 2001 (compare C1 in Fig. 34b with B2 in Fig. 34c). However, these ammonium stocks were essentially only 35% of the April-May values inside Marguerite Bay (Fig. 34b). Throughout the region average ammonium stocks decreased approximately 50% between April-May and July-August (Table 6). Overall, the distribution of ammonium stocks followed that of nutrient deficits for July-August of 2001. The regions of high ammonium stocks (B2 and C2 in Fig. 34c) were co-located with the regions of high nutrient deficits (B2 and C2 in Fig. 16a, b). The regions of the lowest ammonium stocks characterized by ammonium stock values <0.05 mol m$^{-2}$ were found in the northeastern parts of the study area (A2) and in the southwestern offshore part (Fig. 34c) and coincided with the locations of the lowest nutrient deficit values (Fig. 16a, b). As mentioned, those locations were the sites of upwelling of deeper waters to the surface during July-August 2001, and concentrations of ammonium in the deep waters were undetectable.

In September-October of 2001, ammonium stocks were essentially zero at most of the sampling locations, except two inner most stations inside Marguerite Bay (see Fig. 1d
for the location) where they were 0.01 and 0.03 mol m$^{-2}$. These September values were approximately 10-20% of those in July-August in that area (Fig. 34c).

In January of 2002, the distribution of ammonium concentration and standing stocks found by LTER was somewhat similar to that in January of 2001. Vertical distribution of ammonium concentration was distinguished by randomly distributed subsurface maxima up to 5 μM (Fig. 33c). However, the range of ammonium stocks (0.12 to 0.47 mol m$^{-2}$) in January of 2002 showed high and low ends to be higher than those in January of 2001 even though the averages were close (Table 6). As in January of 2001, the distribution of ammonium stocks did not show any pattern in January of 2002. Ammonium stocks were >0.2 mol m$^{-2}$ over most of the area, except the offshore locations of line 200 and at the middle locations of line 300 (Fig. 34d). The highest ammonium stocks (>0.4 mol m$^{-2}$) were found near the southern tip of Adelaide Island (Fig. 33d). This peak of high-ammonium stocks coincided with the highest Def (TIN) and Def (SIL) values (Fig. 20a, b).

In April-May of 2002, the pattern of ammonium concentration distribution found by GLOBEC was similar to that in the previous autumn with the highest concentrations being nearly uniform throughout upper 20-100 m and then rapidly decreasing with depth (Fig. 33d). Ammonium standing stocks ranged from 0.05 to 0.31 mol m$^{-2}$ in April-May of 2002 (Table 6). There were three regions of high ammonium stocks (>0.2 mol m$^{-2}$, A3-C3 in Fig. 34e), but only two were matched by high nutrient deficit regions. The region designated by B3 occupied a portion of the study area from the southern tip of Adelaide Island to the central part of Marguerite Bay (Fig. 34e) and was matched by peaks of the highest Def (TIN) and Def (SIL) values (Fig. 22a, b). The region designated as C3,
located between Alexander and Charcot Islands (Fig. 34e), was matched only by a high
Def (SIL) region (Fig. 22b). However, the region designated as A3 was not matched by
either Def (TIN) nor Def (SIL) peaks (compare Figs. 22a, b and 34e). The lowest
ammonium stocks, <0.1 mol m^{-2}, were found beyond the shelf break (Fig. 34e). In 2002,
there was an overall decrease in average ammonium stocks between January and April-
May (Table 6). As in 2001, there was a decrease of ammonium stocks in the northern part
of the study area between January and April-May of 2002 (compare Figs. 34d and 34e).
However, ammonium stocks near the southern tip of Adelaide Island also decreased—
from 0.4 mol m^{-2} in January (Fig.34d) to 0.3 mol m^{-2} in April-May (Fig. 34e) – that was
not observed in 2001 (Fig. 34a, b).

Another major difference between 2001 and 2002 was that ammonium stocks
observed in April-May of 2002 were lower than those in the previous autumn (compare
Figs. 34b and e). Ammonium stocks in April-May of 2002 were rather comparable with
those found in July-August of 2001 (Fig. 34c). The 2002 April-May ammonium stock
values were similar to those of April-May of 2001 in the middle and outer shelf locations
but were lower than those of April-May of 2001 in the inshore areas (compare Figs. 34b
and 34e). Ammonium stocks observed in the inner part of Marguerite Bay and between
Alexander and Charcot Islands in April-May of 2002 were only 50% of those in April-

In August-September of 2002, ammonium stocks ranged from 0.0 to 0.1 mol m^{-2}
(Table 6). Fig. 34f shows that ammonium stocks in August-September of 2002 were
slightly lower than those found at the same locations in July-August of 2001 (Fig. 34c).
Because ammonium stocks were very low over most of the area sampled in August-
September of 2002, there was no distinct pattern in the stock distribution. However, a region of zero ammonium stocks along the west coast of Adelaide Island was evident (Fig. 34f) and coincided with the lowest deficits of nutrients (Fig. 24a, b).

3.2. **Nitrite dynamics in the Marguerite Bay region in 2001 and 2002.**

Accumulation of nitrite in the upper water column indicates active nitrogen cycling as nitrite is an intermediate product of nitrification — oxidation of ammonium to nitrate — and therefore can be used to elucidate red/ox capacity of the resident microbial communities. Similarly to ammonium, nitrite was observed in the upper 100 m of the water column and was generally undetectable in the deep waters of the Marguerite Bay region in 2001 and 2002.

In January of 2001 and 2002, nitrite stocks integrated from surface to the depth of zero nitrite were generally 0.01-0.06 mol m\(^{-2}\) (Table 6). Nitrite concentrations were typically the highest near the surface; no distinctive subsurface nitrite maxima were observed (not shown). It is likely that the observed nitrite did not result from the ammonium oxidation as nitrification is inhibited by light (Olson, 1981). Nitrite also can be released during nitrate assimilation by phytoplankton (Kiefer et al., 1976; Olson, 1981). Overall, nitrite stocks were only 10-15% of the ammonium stocks (Table 6).

In April-May of 2001 and 2002, nitrite stocks were similar to those in January (Table 6). However, a few subsurface maxima in nitrite concentration were observed during April-May of 2001 and 70% of the stations exhibited substantial subsurface maxima in nitrite during April-May of 2002 that might indicate some regeneration of nitrite through nitrification. Moreover, nitrite stocks were positively correlated with
ammonium stocks ($r^2=0.41$ for April-May 2001 and $r^2=0.48$ in April-May 2002) suggesting that production of nitrite was dependant on availability of ammonium.

Nitrite stocks reduced proportionally to the decrease in ammonium stocks between autumns and winters of 2001 and 2002 (Table 6). For example, in September-October of 2001, nitrite was present only at those locations where detectable ammonium stocks were observed. Low irradiance levels in the wintertime could well have permitted nitriifying bacteria to oxidize the ammonium to nitrate since photoinhibition of their activity should have been reduced (Olson, 1981). However, magnitude of the nitrification is unclear.

To sum up, there was little indication of nitrification during the summer-time surveys in 2001 and 2002. Some evidences of nitrification were found for the autumnal surveys in both years. The presence of nitrite in the upper water column during the winter-time surveys might suggest the occurrence of some nitrification. The magnitude of this process cannot be ascertained just from the relative distribution of nitrite and ammonium. However, nitrification rates measured in the Antarctic coastal waters appear to be very low—less than a few nM d$^{-1}$ (Olson et al., 1981; Priscu et al., 1990; Karl et al., 1996).

3.3. Ammonium sources

There were significant differences in amount and distribution of ammonium between the seasons and between the two years. As ammonium was generally an upper water column phenomenon, the presence of ammonium and variability in the distribution of ammonium concentrations and stocks in the upper 100-200 m was related to biological and physical processes in the upper water column. Ammonium concentration exhibited
subsurface maxima in the summer time and was uniform throughout the upper 30-100 m in autumn and mid-winter in both years. Summer time subsurface maxima in ammonium concentration likely resulted from preferential ammonium remineralization at those depths and/or larger ammonium uptake near the surface and lesser uptake deeper in the water column as most of the phytoplankton biomass was positioned in the upper 40-60 m of the water column in January of 2001 and 2002 (Vernet, 2001, 2002). By autumn reduced uptake by phytoplankton and dispersion due to enhanced vertical mixing resulted in the nearly uniform distribution of ammonium concentration in the mixed-layer.

In both January of 2001 and 2002, ammonium stocks exhibited patchy distributions that seemed to be unrelated to NCP and nutrient deficits ($r^2=0$) or to physical properties ($r^2<0.4$). This suggests that ammonium production was regulated by heterotrophic and/or bacterial activity, which was apparently not related to the environmental conditions or net community production (i.e., nutrient deficits).

In January of 2001, macro- and mesozooplankton biomass sampled with 2-m$^2$ trawl from the surface to 120 m depth (Ross and Quetin, 2001) showed the highest values up to 35.6 g wet wt m$^{-2}$ at the offshore locations (Fig. 35) and was generally low throughout the rest of the study area (2.33±1.82 g wet wt m$^{-2}$). The locations of high zooplankton biomass were dominated by *Salpa thompsoni* (>75%). Biomass of Antarctic krill, *Euphausia superba*, was <6.0 g wet wt m$^{-2}$ throughout the study area and contributed to 32±26% of the total zooplankton biomass. There was no apparent correlation ($r^2<0.1$) between ammonium stocks and total zooplankton biomass and dominant zooplankton species (*Salpa thompsoni* and *Euphausia superba*) and zooplankton biomass was too low to produce all the ammonium stocks observed.
Fig. 35. Distribution of the macrozooplankton biomass collected from 2-m² metro trawl towed obliquely between the surface and 120 m in January of 2001. Units are in mg m⁻³.

For example, total zooplankton biomass integrated from the surface to 120 m of 6.23 g wet wt m⁻² observed in Marguerite Bay in January of 2001 should have had ammonium production rate of 0.24 mmol (NH₄) m⁻² d⁻¹. This production rate was obtained by using an ammonium excretion rate for mixed zooplankton of 1.6 μmol (NH₄) (g wet wt)⁻¹ h⁻¹, given by Biggs (1982). With this production rate it should have taken more than a year to produce the ammonium standing stocks observed in Marguerite Bay in January of 2001 (0.26 mol m⁻²), which is unreasonable. However, some considerations should be taken into account. First, the zooplankton biomass values presented here came from the upper 120 m of the water column and cannot account for ammonium production of zooplankton from deeper parts of the water column. However, a deeper trawl, from the surface to 300 m deep, was towed at some stations in January of 2001. Zooplankton
biomass from the deep trawls was <26.3 g wet wt m\(^2\) and suggests that the contribution to ammonium production from deep zooplankton was insignificant. Also, Lascara et al. (1999) found <25% of the total zooplankton biomass below 50 m in summer time on the WAP continental shelf. Second, mobile zooplankton such as krill, might avoid nets (Biggs, 1982; Atkinson et al., 2001). Third, zooplankton biomass might have been greater earlier in the season before the time of sampling in January of 2001. If any significant temporal increase in zooplankton biomass had occurred before January of 2001 it might be apparent in relative distributions of nutrient deficits, particularly Def (SIL) (it has been shown that the study area was dominated by diatoms in January of 2001), and chlorophyll \(a\). Presence of high zooplankton biomass would have led to extensive grazing on phytoplankton, which, in turn, would have reduced chlorophyll \(a\) concentration but should have not affected silica deficit as there is little silica remineralization in the upper water column (DeMaster et al., 1996).

![Diagram](image_url)

**Fig. 36.** Relationship between the average euphotic zone chlorophyll \(a\) concentration (mg m\(^{-3}\)) and silica deficit (mol m\(^3\)) in January of 2001.
Relationship between Def (SIL) and average chlorophyll a concentration for January 2001 LTER data (Fig. 36) encourages dividing the study area in two zones. Zone I with significant correlation between chlorophyll a and silica deficit (filled circles; n=20, \( r^2=0.90 \)) was characterized by generally low ammonium stocks (<0.2 mol m\(^{-2} \) in Fig. 34a) but, however, included Marguerite Bay and the inner portion of line 400 with ammonium stocks of \(~0.25 \) mol m\(^{-2} \) (Fig. 34a). Zone II was characterized by low chlorophyll a concentration (<1 mg m\(^{-3} \)) and elevated silica depletion (open circles in Fig. 34), it covered the remaining part of the study area with ammonium stocks >0.2 mol m\(^{-2} \) in Fig. 34a. The correlation between chlorophyll a concentration and silica deficit suggests little impact from grazing on phytoplankton in zone I. By contrast, it is likely that a grazing event had occurred during the period from the early spring to January in zone II producing the ammonium stocks observed.

In January of 2002, zooplankton biomass was somewhat higher than that in January of 2001 (Fig. 37). The average biomass was 7.6±9.7 g m\(^{-2} \) (Ross and Quentin, 2002). Salps were abundant only at some offshore locations during January of 2002. Krill dominated zooplankton community over most of the study area including the locations of the highest zooplankton biomass. Moreover, a swarm of *Euphausia superba* with biomass of \(~200 \) g m\(^{-2} \) and krill density of \(~700 \) ind. m\(^{-2} \) was observed in the middle portion of the LTER study area (Ross and Quentin, 2002).

In January 2002, the highest ammonium stocks (>0.4 mol m\(^{-2} \) in Fig. 34d) were located at the entrance to Marguerite Bay. Since zooplankton biomass was \(~6.0 \) g m\(^{-2} \) at that location (Ross and Quentin, 2002), it might have produced 0.23 mmol NH\(_4\) m\(^{-2} \) d\(^{-1} \) assuming zooplankton ammonium excretion rate of 1.6 \( \mu \)mol NH\(_4\) (g wet wt\(^{-1} \)) h\(^{-1} \) (Biggs,
Fig. 37. Distribution of the macrozooplankton biomass collected from 2-m³ metro trawl towed obliquely between the surface and 120 m in January 2002. Units are in mg m⁻³. Filled circle indicates the location of a krill swarm (~700 ind. m⁻²).

1982). This rate was too low to account for the accumulated ammonium stocks. Yet, the region of the highest ammonium stocks (Fig. 34d) coincided with the peaks of the highest nutrient deficits (Fig. 22a, b) and a peak of the euphotic zone average phaeopigments concentration (> 20 mg m⁻³, Fig. 29b). Phaeopigments result from break down of chlorophyll a by zooplankton grazing (DiTillio and Smith, 1996). The presence of high concentrations of phaeopigments at the locations of the highest nutrient deficits and relatively low chlorophyll a concentration (Fig. 29a) suggested a possible recent grazing by krill swarm observed not very far from Marguerite Bay (Fig. 37). Indeed, assuming ammonium excretion rate of Biggs (1982) it would have taken only 5 days for the krill swarm to produce the ammonium stocks of 0.4 mol NH₄ m⁻². In addition, high biomass
bacterial communities were found in association with krill events in other areas of the Southern Ocean (Goeyens et al., 1991). Goeyens et al. (1991) found that krill may not contribute in a direct way to the ammonium pool but instead probably initiate the bacterial breakdown of debris. Thus, presence of krill swarm might have been related to the high ammonium stocks observed at the entrance to Marguerite Bay in January of 2002.

Overall, macro- and mesozooplankton seemed to play different roles in the production of ammonium stocks in January 2001 and January 2002. In January 2001, if any contribution to the ammonium pool by macro- and mesozooplankton had occurred it would have been in the generally low-productive areas of the outer shelf and in the northwestern part of the study area. The occurrences of elevated zooplankton in those areas might be related to the UCDW intrusions (see Fig. 9a for the distributions of the potential temperature maximum in January of 2001) as it has been suggested by Prezelin et al. (2000) and/or to the retention within a gyre that occupied the northern part of the study area (Klinck et al., 2004). However, there was no evidence of abundant macro- and mesozooplankton in the regions of high phytoplankton biomass in January 2001. An alternative explanation of the elevated ammonium stocks observed in those regions in the summer of 2001 was the activity of smaller heterotrophic plankton (excretion, sloppy feeding) and bacterial remineralization of organic material. Although such data are not available for these field studies, it would be consistent with the observations of Glibert et al. (1982), Koike et al. (1986), Goeyens et al. (1991), Semeneh et al. (1998), Karl et al. (1996 and references therein), and Bode et al. (2002) who found heterotrophic microplankton to be responsible for up to 80% of ammonium stock production on the
WAP shelf and in other Antarctic waters. By contrast, the occurrence of a dense krill swarm in the study area might have been a possible cause for the observed high ammonium stocks during January 2002.

The decrease in ammonium stocks in the northern part of the study grid between January and April-May of both years resulted from a variety of processes that might have taken place during three months elapsed between the surveys: uptake by phytoplankton and/or bacteria, mixing with low-ammonium waters, etc. A positive correlation between ammonium stocks and NCP ($r^2=0.56$ for April-May of 2001 and $r^2=0.41$ for April-May of 2002) was observed in the autumns of 2001 and 2002. In fact, the locations of the regions of high nutrient deficits and high ammonium stocks were the same in April-May of 2001 (A1-E1 in Figs. 16a, b and 34b). April-May of 2002 somewhat followed the trend: the location of the highest ammonium stocks (B2 in Fig. 34e) matched the location of the highest nutrient deficit peaks and C2 was matched by a peak of Def (SIL), but there was no other distinct peak of nutrient deficits corresponding to the ammonium stocks peak A2 (Figs. 34e and 22a, b). Overall, this suggests an extended role of the net biological activity during the growing season into the fall in 2001 and 2002. The higher the nutrient deficits were, the more organic matter should have accumulated. Greater abundances of organic matter in Marguerite Bay in 2001 and 2002 and along the inner shelf in 2001 during the growing seasons should have led to a greater degree of bacterial ammonification in those areas, thus producing the observed ammonium maxima.

Possible contribution of macro- and mesozooplankton to the ammonium pools observed in autumns of 2001 and 2002 can be investigated using the results of MOCNESS tows conducted during the autumnal GLOBEC surveys. Zooplankton
biomass sampled at one offshore, four mid-shelf locations and one in Marguerite Bay in April-May of 2001 (Ashjian et al., 2004) was higher than that in January of 2001. However, in April-May of 2002 zooplankton biomass was sampled from the surface to the bottom and the largest portion of the water column zooplankton (>60%) was positioned below 100 m making comparison a bit difficult. Overall, zooplankton biomass was lower offshore (~10 g wet wt m\(^{-2}\)), moderate on the mid-shelf (~20 g wet wt m\(^{-2}\)) and relatively high inside and along the coast south of Marguerite Bay (130 and 64 g wet wt m\(^{-2}\), respectively) (data from Ashjian et al., 2004). Abundant copepods and less abundant but large euphausiids were 62-93% of the total zooplankton biomass (Ashjian et al., 2004). An offshore/inshore increasing gradient in zooplankton biomass was also evident from backscattering data (Lawson et al., 2004) and was similar to that of ammonium stocks (Fig. 34b). This apparent correlation between zooplankton biomass and ammonium stocks might suggest that the accumulation of the ammonium pool could be due to ammonium excretion by zooplankton. When taking into account the maximal net zooplankton biomass of 130 g wet wt m\(^{-2}\) that was observed in Marguerite Bay in April-May of 2001 (Ashjian et al., 2004) integrated from the surface to the bottom (~600 m), its contribution to the ammonium pool would be 5 mmol NH\(_4\) m\(^{-2}\) d\(^{-1}\). This production rate was obtained by using the ammonium excretion rate of 1.6 \(\mu\)mol NH\(_4\) m\(^{-2}\) h\(^{-1}\) for mixed zooplankton from Biggs (1982). This production rate could produce the range of ammonium standing stocks in Marguerite Bay in April-May of 2001 (Fig. 34b) in 70-100 days, which is not unreasonable. However, the vertical distributions of ammonium and zooplankton did not correlate well. As mentioned, the highest ammonium concentrations were found in the upper 30-70 m of the water column, while most of the zooplankton
biomass was found below the pycnocline (Ashjian et al., 2004). The vertical migration of zooplankton was not clearly evident; so I cannot be certain that they were responsible for the production of high ammonium stocks.

In April-May of 2002, preliminary estimations of zooplankton abundance and biomass from MOCNESS tows and backscattering indicated a considerable reduction (~60%) relative to those in April-May of 2001 (Wiebe et al., 2002b). This argues for a relatively small contribution of macro- and mesozooplankton to the ammonium pool. Moreover, ammonium stocks were reduced approximately 30% between January and April-May of 2002 (Table 6), suggesting that ammonium removal by planktonic organisms and mixing with surrounding low-ammonium waters was greater than any ammonium production during that period.

3.4. Regeneration

Depletions of TIN observed through summer to autumn can be used as an estimate of the magnitude of net community accumulation of the organic matter whereas accumulation of ammonium stocks reflects net seasonal regeneration of organic matter in the upper water column.

In January of 2001 and 2002, the relative proportions of organic matter regenerated in the upper water column ([\(NH_{4ST}\)] / [\(NH_{4ST} + Def\) (TIN)]) were 0.28±0.07 and 0.30±0.08, respectively. As the growing season proceeded in both years accumulated ammonium could be used as a source of nitrogen by phytoplankton, i.e. regenerated production opposite to new production based on nitrate, following the concepts of Eppley and Peterson (1979). A number of studies in the Southern Ocean concluded that utilization of nitrate decreases during the summer season and ammonium prevails in
nitrogen uptake (Olson, 1980; Glibert et al., 1982; Rönner et al., 1983; Koike et al., 1986; Goeyens et al., 1991; Owens et al., 1991; Bury et al., 1995; Bode et al., 2002). The importance of the regenerated production between summers and autumns of 2001 and 2002 can be ascertained from the comparison of $\Delta Si/\Delta N$ and $\Delta Si/\Delta P$ observed in January and April-May of 2001 and 2002. $\Delta Si/\Delta N$ (mean ± 1S.D.) and $\Delta Si/\Delta P$ (mean ± 1S.D.) ratios were 1.6±0.4 and 17.3±5.9, respectively, in January of 2001 and were 1.7±0.4 and 19.3±5.3, respectively, in January of 2002. $\Delta Si/\Delta N$ and $\Delta Si/\Delta P$ ratios increased considerably by the following autumns being 3.7±0.9 and 46.3±9.7, respectively, in April-May of 2001 and 3.8±0.9 and 43.5±9.2, respectively, in April-May of 2002. Labile soft-tissue nitrogen and phosphorus are more likely to be remineralized in the upper water column, while hard-tissue silica is more likely to be exported from the upper mixed-layer (DeMasters et al., 1996; Nelson et al., 1996). Thus since little silica is remineralized in the Antarctic surface waters (DeMasters et al., 1996), phytoplankton may utilize regenerated nitrogen and phosphorus but can use only new silica. The observed two-fold increase in the $\Delta Si/\Delta N$ and $\Delta Si/\Delta P$ deficit ratios between January and April-May of 2001 and 2002 suggested that approximately a half of the primary production during the growing seasons of 2000-2001 and 2001-2002 might have been based on regenerated nutrients in the Marguerite Bay region.

Since POM and DOM typically return to the pre-bloom values by autumn (Sweeney et al., 2000b), organic matter accumulated during the growing season should have been either regenerated in the surface layer or exported from the surface layer. Autumnal depletions of nutrients are good approximations of the exported organic matter (Sweeney et al., 2000b). In April-May of 2001 and 2002, the relative proportions of
organic matter regenerated in the upper water column ([NH\textsubscript{4ST}] / [NH\textsubscript{4ST} + Def (TIN)] were the same on average: 0.27±0.09 and 0.27±0.07, respectively (t-test, p>0.9). In both autumns there was a considerable mesoscale variability in the [NH\textsubscript{4ST}] / [NH\textsubscript{4ST} + Def (TIN)] in the study area ranging from 0.15 to 0.5 in April-May of 2001 and from 0.15 to 0.45 in April-May of 2002. Overall, inshore and mid-shelf regions had [NH\textsubscript{4ST}] / [NH\textsubscript{4ST} + Def (TIN)] values were 0.30±0.10 and 0.30±0.07 in autumns of 2001 and 2002, respectively. The lowest values (0.20±0.08) were observed in the northwestern part of the study area in both autumns of 2001 and 2002 and in the region of the shelf break curvature in the autumn of 2001. Those were the regions of two biogeochemical regimes – outer shelf influenced by UCDW intrusions and the gyre region – identified previously. The low [NH\textsubscript{4ST}] / [NH\textsubscript{4ST} + Def (TIN)] values observed in the gyre region were most likely due to the occurrence of the late phytoplankton blooms in autumns of 2001 and 2002. It was likely that organic matter was not completely remineralized by the time of sampling in this region that resulted in low [NH\textsubscript{4ST}] / [NH\textsubscript{4ST} + Def (TIN)] values.

Thus overall, ~30% of the organic matter accumulated during the growing season was regenerated in the surface layer and ~70% was exported from the upper water column by the end of the growing seasons during both years. The relative proportions of organic matter regenerated in the upper water column by the end of the growing seasons of 2000-2001 and 2001-2002 seemed to be consistent, despite the fact that the magnitude of NCP decreased somewhat between the two years.

3.5. **Seasonal variability in ammonium**

Both physical and biochemical processes could have produced the winter decline in ammonium concentrations and stocks. High ammonium waters in the mixed layer near
the coastline can be diluted by horizontal mixing with offshore low-ammonium waters and/or vertical mixing with deeper low-ammonium waters from below the mixed layer. As it has been mentioned, ice cover and low irradiance levels in the wintertime should have reduced photoinhibition of nitrification activity (Olson, 1981) but, despite this fact, nitrification rates measured in the Antarctic coastal waters were found to be low (Olson et al., 1981; Priscu et al., 1990; Karl et al., 1996). Nevertheless, nitrite dynamics indicates that nitrification did occur in the study area at least during autumn and winter; however, the nitrification rates cannot be ascertained. Metabolic studies on bacterial nitrification in the region are needed to resolve this issue. Another possible sink for ammonium, uptake by phytoplankton, was small because primary production is negligible on WAP continental shelf in austral autumn and winter (Prézelin et al., 2004).

Relationships between ammonium and other properties showed a significant degree of linearity, e.g. the ammonium-salinity relationship for autumns and mid-winters of 2001 and 2002 (Fig. 38). Water with high salinity had low ammonium concentration while, as water became fresher, the concentration of ammonium increased in an inverse, roughly linear proportion. Consistent linearity and consistency of the slopes of this relationship between autumn and winter of both years (t-test, p=0.3 for 2001 and p=0.54 for 2002) suggests that ammonium distribution was largely controlled by physical processes during the autuminal and winter seasons in the study area in 2001 and 2002 and the decrease in ammonium between autumns and winters was largely due to mixing.

The hypothesis that a decrease in ammonium between autumn and winter resulted largely from vertical mixing was tested with a simple model of nutrient fluxes across the seasonal pycnocline between April-May and July-August of 2001. Nutrient flux (Y-flux)
Figure 38. Relationship between salinity and ammonium concentration (µM) in the mixed-layer in (a) April-May (open circles; $R^2=0.85$, [salinity] = -0.18 (±0.01) [NH$_4$] + 33.90 (±0.03)) and July-August (filled circles; $R^2=0.71$, [salinity] = -0.20 (±0.02) [NH$_4$] + 34.01 (±0.02)) of 2001 and (b) April-May (open circles; $R^2=0.54$, [salinity] = -0.30 (±0.03) [NH$_4$] + 34.03 (±0.02)) and August-September (filled circles; $R^2=0.47$, [salinity] = -0.28 (±0.04) [NH$_4$] + 34.07 (±0.02)) of 2002.
was calculated as $Y_{-flux} = k \cdot dY/dz$, where $k$ was vertical diffusivity coefficient, $dY/dz$ was nutrient gradient across seasonal pycnocline, and $dz$, thickness of the pycnocline, was approximated as 50 m. The changes in the nutrient concentration in the upper mixed-layer ($\Delta Y$) were calculated as $\Delta Y = -Y_{flux} / z_{ML}$, where $z_{ML}$ is the average depth of the mixed-layer. The average mixed-layer ammonium concentrations observed in April-May of 2001 were set as the initial values. The deep water ammonium concentration value was set to be zero. The calculations were made for 90 days elapsed between April-May and July-August of 2001.

The vertical diffusivity coefficients of $1.0 \times 10^{-4}$ m$^2$ s$^{-1}$ and $0.36 \times 10^{-4}$ m$^2$ s$^{-1}$ for heat and salt, respectively, were reported by Klinck (1998) from the WAP continental shelf. However, the most recent study by Klinck et al. (2004) in the Marguerite Bay region in autumn and winter obtained a vertical heat diffusivity coefficient of $7 \times 10^{-4}$ m$^2$ s$^{-1}$ which is 7 times the value of Klinck (1998). Thus, for these calculations a vertical salt diffusivity coefficient of $2.52 \times 10^{-4}$ m$^2$ s$^{-1}$, 7-fold greater than that of Klinck (1998) was chosen. The validity of this coefficient was tested by comparing calculation results of the April-May 2001 to July-August 2001 changes of salinity, phosphate, and nitrate with field data obtained in July-August of 2001. The results of the calculations, average mixed-layer salinities (33.6 – 34.0, average 33.8), nitrate concentrations (23.5 – 30.1 µM, average 26.6 µM), and phosphate concentrations (1.77 – 2.13 µM, average 1.93 µM), were not statistically different from the average mixed-layer salinities (33.6 – 34.1, average 33.8), nitrate concentrations (23.5 – 30.8 µM, average 27.3 µM), and phosphate concentrations (1.73 – 2.16 µM, average 1.93 µM) observed in July-August 2001 (t-test for mean, p>0.9).
The calculation results for the average mixed-layer ammonium concentrations showed the range of 0.35 – 2.58 μM with the average of 1.23 μM. However, field data showed slightly lower values with the range of the mixed-layer ammonium concentrations being 0.03 – 2.21 μM and the average being 0.89 μM. As the calculations accounted only for vertical diffusive mixing, they underestimated the total decrease in ammonium concentrations resulted from upwelling of deep zero-ammonium waters to the surface observed at two locations in the study region and lateral mixing of low-ammonium offshore waters with high-ammonium inshore waters. Nevertheless, the calculations suggested that the losses of ammonium between April-May 2001 (NH₄<sub>average</sub> = 2.2 μM) and July-August 2001 due to vertical mixing were substantial (~45%). Field data showed that the average mixed-layer ammonium concentrations decreased by 60% between autumn and winter. Thus, if any uptake of ammonium by bacteria and/or phytoplankton occurred between autumn and winter, it should have been <25% of the total losses in ammonium. Assuming that this 25% of the decrease in ammonium was a result of nitrification, nitrification rate should have been 4 nM d<sup>-1</sup>, which is in agreement with the results reported by Olson (1981), Priscu et al. (1990), and Karl et al. (1996).

A possible compensation of the ammonium losses due to the mixing by ammonium production by zooplankton, microzooplankton, and bacteria was most likely negligible. For example, in July-August of 2001 total water column zooplankton biomass sampled at the same locations as in April-May of 2001 decreased to the average of 15.2 g wet wt m<sup>-2</sup> from being 43.5 g wet wt m<sup>-2</sup> on average in April-May (Ashjian et al., 2004). Moreover, zooplankton biomass was very low (<2 g wet wt m<sup>-2</sup>) in the upper 100 m of the water column (Ashjian et al., 2004). This suggests little production of ammonium by
zooplankton in winter of 2001. Activities of bacteria and microzooplankton were likely negligible as well: DOM and POM are typically very low in winter (Sweeney et al., 2000b).

To sum up, the decrease in mixed-layer ammonium between autumn and winter in the Marguerite Bay region apparently resulted mostly from the vertical mixing with low-ammonium deep waters with a small but significant contribution of biological uptake (<25%), presumably nitrification with a rate of few nM per day.

3.6. Summary

Overall, ammonium in the Marguerite Bay region had some interesting features. Its high mixed-layer concentrations fell within the range found in high-latitude oceans elsewhere (Smith, 1991; Whittlestone et al., 1986, Gordon et al., 2000; Koike et al., 1986). Yet the changes in ammonium concentration generally run opposite to those of other nutrients. Upper water column concentrations of other nutrients (nitrate, phosphate, and silica) are higher in winter than in summer and autumn; whereas winter ammonium concentrations in the surface layer are much lower than in summer and autumn.

Ammonium stocks reached 0.20±0.08 mol m⁻² by January of 2001 and 0.25±0.09 mol m⁻² by January of 2002. Distribution of ammonium stocks was independent of the NCP and hydrographic properties during both Januaries and seemed to have come from two sources: excretion by larger zooplankton in the low productive regions of outer shelf and northwestern part of the study area influenced by UCDW intrusions onto the shelf and microbial communities associated with phytoplankton bloom in the highly productive nearshore areas. Yet, a presence of a krill swarm in the study area might have been a cause of high ammonium stocks during January 2002. Regenerated ammonium played an
important role in nitrogenous nutrition of phytoplankton in the study area – at least half of the primary production was based on ammonium during the 2000-2001 and 2001-2002 growing seasons.

High ammonium stocks were observed in April-May of 2001 (0.22±0.14 mol m⁻²) and April-May of 2002 (0.16±0.06 mol m⁻²) in the Marguerite Bay area. In contrast to the January distributions, the maximum autumnal standing stocks of ammonium were found at the same locations as the maximum autumnal deficits of other nutrients. These features are found even when comparing ammonium (associated with tissues) to silica, which is associated with frustules. These relationships between regeneration and accumulation of organic matter suggest an extended role of microbial plankton activity during the growing seasons and following demise of the blooms in 2001 and 2002. However, increased biomass of macro- and mesozooplankton from summer to autumn might have contributed to the production of ammonium in 2001. 30% of the net organic matter accumulated during the growing seasons in the Marguerite Bay region was regenerated in the upper water column in 2001 and 2002.

The decline in ammonium stocks between autumn to winter was largely due to mixing with zero- ammonium waters from below the pycnocline. Nitrification was likely to occur in the Marguerite Bay region during autumn and winter of 2001 and 2002 with a rate of few nM per day.

4.1. Introduction

Marguerite Bay, on the West Antarctic Peninsula (WAP), is a highly productive coastal system. It is typically characterized by high primary production with chlorophyll \( a \) concentrations of 12-20 mg chl \( a \) m\(^{-3}\) inside Marguerite Bay during summer months (Karl et al., 1992; Garibotti et al., 2003a, b, 2005). High secondary production is also favored (Ashjian et al., 2004; Lawson et al., 2004). Every spring and summer Marguerite Bay is covered by a seasonal ice zone (SIZ) (Karl et al., 1992; Smith et al., 1998). The melt water from the receding ice brings stability to the upper water column, enhancing primary production. For example, Fig. 39 shows the progression of the Marguerite Bay bloom in summer of 1992 (Dore, per. com.): development of high chlorophyll \( a \) stocks; large depletion of nitrate within the upper 20 m of the water column; and increase in concentration of regenerated nitrogenous nutrients (ammonium and nitrite) with increasing distance (and time) from the ice edge. However, the large influence of sea ice dynamics on primary production of the WAP makes the productivity subject to a relatively large interannual variability (Smith et al., 1998; Quentin and Ross, 2003).

Net community production (NCP) expressed as nutrient depletion in the upper water column was calculated for Marguerite Bay and the surrounding area for autumns of 2001 and 2002 (see Chapter 1). There were significant changes in the magnitude of the nutrient depletion between two autumns. The largest changes, namely a decrease in nutrient deficits from autumn of 2001 to autumn of 2002 (Table 7, Figs. 13a, b and 22a, b), were observed within Marguerite Bay.
Fig. 39. Vertical distribution of (A) chlorophyll $a$ (mg m$^{-3}$), (B) nitrate ($\mu$M), (C) ammonium ($\mu$M), and (D) nitrite ($\mu$M) concentrations along the transect perpendicular to the retreating ice edge during RACER 3 cruise to Marguerite Bay (Dore et al., 1992). Data are courtesy of J. Dore.

The most plausible explanation for the decrease of NCP in Marguerite Bay from one year to another (Table 7) is the effect of different environmental conditions between two years. The 2001-2002 austral year was colder and was characterized by greater sea ice extent than the austral year of 2000-2001 (Figs. 31 and 32). In 2001-2002, the delay in melting of sea ice formed during winter of 2001 and early start in new ice formation in fall of 2002 resulted in shorter period of ice-free conditions favorable for phytoplankton growth than in 2000-2001. Shorter period of phytoplankton growth led to lesser nutrient uptake and therefore lesser nutrient deficits by the end of the growing season (autumn) in 2002 than in 2001.
Table 7. Deficits (mean± 1 S.D.) of total inorganic nitrogen (Def(TIN)), of phosphate (Def(PO₄)), and of silica (Def(SIL)), Net community production (NCP) and ammonium stocks (NH₄ST) for Marguerite Bay. Marguerite Bay is defined as the area between Adelaide and Alexander Islands and the coast of Antarctic Peninsula (Fig. 1) during April-May 2001 and April-May 2002. All units are mol m⁻²

<table>
<thead>
<tr>
<th></th>
<th>Def(TIN)</th>
<th>Def(PO₄)</th>
<th>Def(SIL)</th>
<th>NCP</th>
<th>NH₄ST</th>
</tr>
</thead>
<tbody>
<tr>
<td>April-May 2001</td>
<td>0.90±0.30</td>
<td>0.07±0.03</td>
<td>3.6±1.2</td>
<td>6.3±2.1</td>
<td>0.40±0.08</td>
</tr>
<tr>
<td>April-May 2002</td>
<td>0.53±0.21</td>
<td>0.05±0.02</td>
<td>2.1±1.1</td>
<td>3.7±1.5</td>
<td>0.21±0.07</td>
</tr>
</tbody>
</table>

Similarly, a decrease in ammonium standing stocks was observed in Marguerite Bay between autumn of 2001 and autumn of 2002 (see Chapter 2). Ammonium stocks integrated from the surface to the depth of zero ammonium concentration in autumn of 2002 were approximately one half of those in autumn of 2001 (Table 7).

There could be several explanations for such decrease in ammonium stocks. First, a difference in the biomass of zooplankton, primarily krill and copepods. They are known to be important sources of ammonium in the Antarctic waters (Owens et al., 1991). Indeed, zooplankton biomass in autumn of 2001 was considerably greater than that in the autumn of 2002 in Marguerite Bay (Ashjian et al., 2004; Ashjian, per.comm.).

The second explanation for the decrease in the ammonium concentrations and stocks is derived from a hypothesis that bacteria play a major role in the ammonium production in the Antarctic coastal waters. For example, Tupas et al. (1994) found 27-55% of the total ammonium in the upper water column to be remineralized by bacteria. Dissolved organic matter (DOM) is a primary substrate for bacteria and phytoplankton are often the major producers of DOM. Thus, a decrease in net primary production
between the 2000-2001 and 2001-2002 austral years (Table 7), might have led to a decrease in DOM availability to bacteria, and therefore in bacterial ammonification.

And the third possible explanation for the decrease in ammonium pool between two years is more active nitrification, i.e. bacterially mediated oxidation of ammonium to nitrite and nitrate, during the austral year of 2001-2002 than in 2000-2001. The 2001-2002 year was characterized by the late retreat and early advance of the sea ice cover. Ice cover restricts light penetration to the water column – a condition unfavorable for phytoplankton growth, but favorable for nitrifying bacteria, since nitrification is light-inhibited (Olson, 1980). Thus, greater ice cover in 2001-2002 could have allowed nitrifying bacteria to oxidize more ammonium during that year than in 2000-2001.

In Chapter 2 it was shown that the field data collected during the SO GLOBEC and LTER surveys were inconclusive about which processes led to the build up and interannual variability of ammonium stocks in 2001 and 2002. Thus, the role of sea ice dynamics, phytoplankton growth factors, and bacterial and zooplankton stock variability between two years were examined with a quasi-two dimensional model. It investigates cycles of nitrogen and carbon through the dissolved inorganic nutrient pool (ammonium, nitrate, and DIC), three groups of phytoplankton, bacterioplankton, zooplankton fecal pellets, and dissolved organic matter (DOM) (Fig. 40). The model used for this study was a modification of the numerical model developed by Walsh et al. (1995, 2001).

4.2. Model description

Interactions among the state variables of the model were described by 13 coupled partial differential equations. They were a function of depth due to vertical light attenuation, gravitation, turbulence and water column stability, seasonal and diurnal light
cycles at the sea surface. The equations were marched forward in time with time step of 60 s, starting in the middle of Antarctic winter (August) until the annual cycle was complete.

4.2.1. **Vertical mixing**

The time dependent vertical eddy diffusivity of the water column was obtained from a turbulence closure scheme following Mellor and Yamada (1982). It depended on vertical density structure of the water column and velocity shear driven by winds. To compute the seasonal water column stratification, the temperature and salinity fields observed in 2000-01 and 2001-02 were used (Table 8). Observed seasonal variability in salinity accounted for effects of melt-water and ice-rejected brines on the density fields. Wind stress forcing and density fields were computed daily from interpolated monthly means (Table 8).

4.2.2. **Lateral mixing**

Lateral exchange of the model’s state variables between Marguerite Bay and the offshore waters was parameterized by Fick’s first law with a horizontal eddy mixing coefficient \( K_x \) of \( 1.7 \times 10^7 \text{ cm}^2 \text{ s}^{-1} \) to account for impacts of the ACC.

4.2.3. **Boundary and initial conditions**

Offshore nutrients and chlorophyll showed little seasonal variability, compared to those in the nearshore waters, such that the boundary conditions of the model (Table 9) were obtained from observations within the ACC during SO GLOBEC and LTER surveys. The initial values of nitrate, ammonium and chlorophyll were averages of those observed in Marguerite Bay during July-October of 2001.
Fig. 40. A model structure of the cycles of carbon and nitrogen between pools of atmospheric and marine carbon dioxide, nitrate, ammonium, three competing groups of phytoplankton (diatoms, cryptophytes, and prymnesiophytes), major zooplankton (krill, copepods, and protozoa), bacteria, zooplankton fecal pellets, monomeric (DOC$_1$) and macromolecular (DOC$_2$) dissolved organic carbon regulated by availability of light and mixing regime in Marguerite Bay. The details of the carbon/nitrogen transfers and interactions between model compartments are described in the text.
Table 8. Monthly averages of mixed-layer depth, temperature, salinity, wind speed, and ice cover during the 2000-2001 and 2001-2002 modeled periods. The values are from the data obtained during SO GLOBEC surveys, LTER surveys, and from Meredith et al. (2004). Ice cover data were courtesy of J. Hyatt (WHOI).

<table>
<thead>
<tr>
<th>(a) 2000-2001</th>
<th>Aug</th>
<th>Sep</th>
<th>Oct</th>
<th>Nov</th>
<th>Dec</th>
<th>Jan</th>
<th>Feb</th>
<th>Mar</th>
<th>Apr</th>
<th>May</th>
<th>Jun</th>
<th>Jul</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixed-layer depth (m)</td>
<td>95</td>
<td>100</td>
<td>100</td>
<td>80</td>
<td>20</td>
<td>12</td>
<td>20</td>
<td>28</td>
<td>40</td>
<td>60</td>
<td>65</td>
<td>80</td>
</tr>
<tr>
<td>Mixed-layer temperature (°C)</td>
<td>-1.8</td>
<td>-1.8</td>
<td>-1.5</td>
<td>-1.0</td>
<td>0.0</td>
<td>2.5</td>
<td>2.0</td>
<td>1.0</td>
<td>-0.8</td>
<td>-0.9</td>
<td>-1.5</td>
<td>-1.8</td>
</tr>
<tr>
<td>Mixed-layer salinity</td>
<td>33.8</td>
<td>33.9</td>
<td>34.0</td>
<td>33.8</td>
<td>33.0</td>
<td>32.9</td>
<td>32.9</td>
<td>33.2</td>
<td>33.3</td>
<td>33.4</td>
<td>33.5</td>
<td>33.6</td>
</tr>
<tr>
<td>Wind speed (m s⁻¹)</td>
<td>8.1</td>
<td>8.5</td>
<td>9.0</td>
<td>7.3</td>
<td>6.4</td>
<td>4.5</td>
<td>8.0</td>
<td>5.4</td>
<td>8.7</td>
<td>8.0</td>
<td>8.9</td>
<td>8.6</td>
</tr>
<tr>
<td>Ice cover</td>
<td>0.85</td>
<td>1.0</td>
<td>0.90</td>
<td>0.80</td>
<td>0.40</td>
<td>0.05</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.12</td>
<td>0.16</td>
<td>0.74</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(b) 2001-2002</th>
<th>Aug</th>
<th>Sep</th>
<th>Oct</th>
<th>Nov</th>
<th>Dec</th>
<th>Jan</th>
<th>Feb</th>
<th>Mar</th>
<th>Apr</th>
<th>May</th>
<th>Jun</th>
<th>Jul</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixed-layer depth (m)</td>
<td>80</td>
<td>95</td>
<td>100</td>
<td>100</td>
<td>50</td>
<td>15</td>
<td>20</td>
<td>30</td>
<td>50</td>
<td>50</td>
<td>65</td>
<td>80</td>
</tr>
<tr>
<td>Mixed-layer temperature (°C)</td>
<td>-1.8</td>
<td>-1.8</td>
<td>-1.8</td>
<td>-1.5</td>
<td>-0.5</td>
<td>1.0</td>
<td>0.5</td>
<td>-0.5</td>
<td>-1.0</td>
<td>-1.5</td>
<td>-1.8</td>
<td>-1.8</td>
</tr>
<tr>
<td>Mixed-layer salinity</td>
<td>33.7</td>
<td>33.9</td>
<td>34.0</td>
<td>34.0</td>
<td>34.0</td>
<td>33.5</td>
<td>32.9</td>
<td>33.0</td>
<td>33.1</td>
<td>33.2</td>
<td>33.5</td>
<td>33.6</td>
</tr>
<tr>
<td>Wind speed (m s⁻¹)</td>
<td>8.7</td>
<td>8.5</td>
<td>9.0</td>
<td>7.3</td>
<td>6.4</td>
<td>4.5</td>
<td>7.9</td>
<td>5.4</td>
<td>8.7</td>
<td>4.0</td>
<td>5.0</td>
<td>5.5</td>
</tr>
<tr>
<td>Ice cover</td>
<td>1.0</td>
<td>1.0</td>
<td>0.90</td>
<td>0.83</td>
<td>0.80</td>
<td>0.80</td>
<td>0.31</td>
<td>0.25</td>
<td>0.20</td>
<td>0.55</td>
<td>0.90</td>
<td>0.90</td>
</tr>
</tbody>
</table>
Table 9. The initial and boundary conditions of ammonium (μM), nitrate (μM), dissolved inorganic carbon (μM), diatom (D), nanoflagellate (NF) and prymnesiophytes (Pr) groups of phytoplankton (mg chl a m⁻³), bacteria (mg C m⁻³), and refractory background (DOCᵣ) and labile (DOC₁,₂) dissolved organic carbon (μM) within Marguerite Bay.

<table>
<thead>
<tr>
<th></th>
<th>NH₄</th>
<th>NO₃</th>
<th>ΣCO₂</th>
<th>D</th>
<th>NF</th>
<th>Pr</th>
<th>B</th>
<th>DOCᵣ</th>
<th>DOC₁,₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>1.0</td>
<td>28.0</td>
<td>2225</td>
<td>0.024</td>
<td>0.030</td>
<td>0.010</td>
<td>1.0</td>
<td>40.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Boundary</td>
<td>0.0</td>
<td>31.5</td>
<td>2225</td>
<td>0.024</td>
<td>0.030</td>
<td>0.010</td>
<td>1.0</td>
<td>40.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

No measurements of dissolved organic carbon (DOC) were made during SO GLOBEC and LTER surveys. I thus chose a background refractory DOCᵣ value of 40 μM, since 44±4 μM were found in deep waters of Gerlache Strait (Doval et al., 2002). A similar concentration of 42 μM was measured during late winter in the Ross Sea (Carlson et al., 2000), while 38 μM was observed in deep waters in the Atlantic sector of the Southern Ocean (Kahler et al., 1996). The initial and boundary values of labile DOC₁,₂ were zeros according to autumn and late winter observations in the Ross Sea (Carlson et al., 2000). The initial and boundary conditions for bacterial biomass were from Fritsen (2001) and those of dissolved organic carbon and phytoplankton were from Walsh et al. (2001).

4.2.4. State equations

4.2.4.1. Phytoplankton

Antarctic phytoplankton communities are usually dominated by diatoms or prymnesiophytes (Phaeocystis antarctica). Another major constituent, cryptophytes, tends to bloom in association with glacial melt water (Moline and Prezelin, 1996; Prezelin et al., 2000; Rodriguez et al., 2002; Garibotti et al., 2005). Diatoms tend to dominate phytoplankton biomass in Marguerite Bay (Garibotti et al., 2005). They are a
primary food source for Antarctic crustaceans. Prymnesiophytes, despite their relatively low biomass, often contribute significantly to total primary production due to their relatively high growth rates and adaptation to low irradiance levels. The time dependence of each phytoplankton group \( P_j \) was described with the following equation:

\[
\frac{\partial}{\partial t} P_j = \frac{\partial}{\partial x} K_x \frac{\partial}{\partial x} P_j + \frac{\partial}{\partial z} K_z \frac{\partial}{\partial z} P_j + u_j \text{NO}_3 P_j + u_j \text{NH}_4 P_j - (\psi_j + \varepsilon_j + \gamma_j + \eta_j) P_j - \frac{\partial}{\partial z} w_j P_j
\]  

(1)

The first and second terms of Eq. (1) are the lateral and vertical diffusive fluxes. The third and the fourth terms are the phytoplankton growth terms expressed through carbon equivalents of the nitrate and ammonium uptake during gross photosynthesis. Phytoplankton growth is considered to be unlimited by DIC availability but to be regulated by availability of light and nutrients. Thus, nitrogen uptake by Antarctic phytoplankton is a function of substrate concentration and irradiance. Ammonium and nitrate are generally considered to be the primary nitrogen sources for phytoplankton.

Rate of ammonium and nitrate uptake for each phytoplankton group \( J \) were:

\[
u_j \text{NH}_4 = [\mu_{\text{max}}(J)]*[I(z)/I_s]*(\exp(1-I(z)/I_s))]*[\text{NH}_4/(K_{\text{NH}_4}\text{+NH}_4)]
\]  

(2)

\[
u_j \text{NO}_3 = [\mu_{\text{max}}(J)]*[I(z)/I_s]*(\exp(1-I(z)/I_s))]*[\text{NO}_3/(K_{\text{NO}_3}\text{+NO}_3)]
\]  

(3)

where \( \mu_{\text{max}}(J) \) is the maximal growth rate of phytoplankton group \( J \) (Table 10). A wide range of growth rates have been reported for diatom cultures from the Southern Ocean \((0.25 – 0.7 \text{ d}^{-1}, \text{Jacques (1983)}) \) and natural Antarctic communities \((0.1 – 1.0 \text{ d}^{-1}, \text{Fennel et al. (2003)}) \). In this model the maximum growth rates for diatoms and cryptophytes were set to \( 0.7 \text{ d}^{-1} \), since the maximal growth rate for the latter group may be the same as for diatoms \((\text{Sakshaug and Holm-Hansen, 1986}) \), and \( 0.76 \text{ d}^{-1} \) for prymnesiophytes.
$I(z)$, which is the remnant photosynthetic active radiation (PAR) at depth $z$, was computed from exponential light attenuation by water ($\kappa_w$), by each group of phytoplankton ($\kappa_pP_j$), by bacteria ($\kappa_bB$), and by colored DOC ($\kappa_d$CDOC in Eq. (4a)) of surface irradiance field ($I(0)$).

$$I(z) = I(0) \times \exp \left[ -\left( \kappa_w + \kappa_pP_j + \kappa_bB + \kappa_d\text{CDOC} \right)z \right] \quad (4a)$$

where

$$I(0) = \Phi \times I_p \times \exp \left[ -\kappa_i \zeta \right] + (1 - \Phi) \times I_p \quad (4b)$$

$I(0)$ – surface PAR – is thus a fraction of total incident PAR at 65-70°S, $I_p$, after light loss by ice cover ($\Phi$) of thickness $\zeta$ and attenuation $\kappa_i$. $I_p$ is extrapolated daily from monthly means specified from climatological data by Walsh et al. (2001).

$I_s$ in Eqs. (2) and (3) is the saturation light intensity for maximal growth specific for each phytoplankton group (Table 10). $I_s = 2.72 \times P_{\omega}^{\alpha} \times P_{\omega}^{\alpha} - 1$, where $P_{\omega}^{\alpha}$ is the chlorophyll normalized maximum photosynthetic rate and $\alpha$ is the initial slope of the $P-I$ curve. The $I_s$ value for cultures of Antarctic diatoms calculated from $P_{\omega}^{\alpha}$ and $\alpha$ values measured by Jacques (1983) is 45 W m$^{-2}$, in agreement with the average $I_s = 50$ W m$^{-2}$ for diatom dominated stations in the southern Bellingshausen Sea (Boyd et al., 1995) and $I_s$ values ranging from 37 to 47 W m$^{-2}$ for diatom dominated waters of the northern Bellingshausen sea (Lorenzo et al., 2002). Prymnesiophytes, on the other hand, are shade adapted and have lower $I_s$ values (~25 W m$^{-2}$) than diatoms (Palmissano et al., 1986). Cryptophytes were found to have an intermediate $I_s$ value of ~35 W m$^{-2}$ (Figueiras et al., 1994), compared to higher $I_s$ values for diatoms and lower ones for prymnesiophytes.

Values for half-saturation constants ($K_i$ in Eq. (2) and (3)) were chosen to be 0.87 µM and 0.17 µM for nitrate and ammonium, respectively (Smith and Harrison, 1991).
Table 10. Model parameters of Marguerite Bay plankton communities. The justification for the parameter choice is discussed in section 3.2.4.

<table>
<thead>
<tr>
<th></th>
<th>Diatom</th>
<th>Cryptophytes</th>
<th>Prymnesiophytes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>a) Phytoplankton</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maximum growth rate (d⁻¹)</td>
<td>µ</td>
<td>0.70</td>
<td>0.70</td>
</tr>
<tr>
<td>Fraction of biomass respired</td>
<td>ε</td>
<td>0.01</td>
<td>0.005</td>
</tr>
<tr>
<td>Fraction of growth excreted as DOC₁</td>
<td>ψ</td>
<td>0.13</td>
<td>0.10</td>
</tr>
<tr>
<td>Fraction of biomass autolyzed as DOC₂</td>
<td>η</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>C:Chl a (wt wt⁻¹)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C:N (mol mol⁻¹)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Half-saturation constant of NO₃ uptake</td>
<td>K₅NO₃</td>
<td>0.87</td>
<td>0.87</td>
</tr>
<tr>
<td>Half-saturation constant of NH₄ uptake</td>
<td>K₅NH₄</td>
<td>0.17</td>
<td>0.17</td>
</tr>
<tr>
<td>Saturation intensity for growth (W m⁻²)</td>
<td>Jₛ</td>
<td>45</td>
<td>35</td>
</tr>
<tr>
<td>Specific attenuation coefficient, m² (mg chl a⁻¹)</td>
<td>κₚ</td>
<td>0.024ᵇ</td>
<td>0.012ᵇ</td>
</tr>
<tr>
<td>Grazing threshold (mg chl a m⁻³)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Protozoan grazing rate (mg chl a m⁻³ d⁻¹), γᵣ</td>
<td></td>
<td>--</td>
<td>0.125P</td>
</tr>
<tr>
<td>Sinking velocity (m d⁻¹)</td>
<td>w</td>
<td>0.001P²</td>
<td>0.025</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Adult krill</th>
<th>Juv. krill</th>
<th>Larval krill</th>
<th>Copepods</th>
<th>Protozoa</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>b) Zooplankton</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fraction of grazed POC to DOC₂</td>
<td>ξ</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.0</td>
</tr>
<tr>
<td>Fraction of ingested POC to pellets</td>
<td>ρ</td>
<td>0.35</td>
<td>0.35</td>
<td>0.65</td>
<td>0.35</td>
</tr>
<tr>
<td>Fraction of ingested POC to DIC and NH₄</td>
<td>δ</td>
<td>0.65</td>
<td>0.65</td>
<td>0.65</td>
<td>0.65</td>
</tr>
<tr>
<td>Fraction of ingested POC to omnivores</td>
<td>X₃</td>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pellet sinking velocity (m d⁻¹)</td>
<td>w</td>
<td>500ᵈ</td>
<td>500ᵈ</td>
<td>100ᵈ</td>
<td>100ᵈ</td>
</tr>
<tr>
<td>Fraction of pellet biomass lysed</td>
<td>τ</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
</tbody>
</table>

---

132
### Table 10 (continued).

<table>
<thead>
<tr>
<th>c) Bacterioplankton</th>
<th>Ammonifying</th>
<th>Nitrifying</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum growth rate (d(^{-1}))</td>
<td>(\mu_B)</td>
<td>0.32</td>
</tr>
<tr>
<td>Fraction of growth to DIC and NH(_4)</td>
<td>(\beta)</td>
<td>0.65</td>
</tr>
<tr>
<td>Half-saturation constant of DOC(_{1,2}) uptake</td>
<td>(K_{\text{DOC}})</td>
<td>0.83</td>
</tr>
<tr>
<td>DOC(_2) palatability</td>
<td>(\chi)</td>
<td>0.80</td>
</tr>
<tr>
<td>Mortality rate (d(^{-1}))</td>
<td>(m)</td>
<td>0.06</td>
</tr>
<tr>
<td>Specific attenuation coefficient (m(^2)(mg C(^{-1}))</td>
<td>(\kappa_s)</td>
<td>0.0006 (^b)</td>
</tr>
<tr>
<td>C:N (mol mol(^{-1}))</td>
<td></td>
<td>5.0</td>
</tr>
<tr>
<td>Nitrification rate ((\mu)M d(^{-1}))</td>
<td>(X_1)</td>
<td>0.02</td>
</tr>
<tr>
<td>Nitrification threshold ((\mu)M)</td>
<td></td>
<td>0.01</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>d) Other parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Attenuation of sea water (m(^{-1}))</td>
<td>(\kappa_w)</td>
</tr>
<tr>
<td>Attenuation of ice/snow</td>
<td>(\kappa_i)</td>
</tr>
<tr>
<td>Specific attenuation coefficient of CDOC (m(^2)(mg DOC(^{-1}))</td>
<td>(\kappa_d)</td>
</tr>
<tr>
<td>Assumed ice/snow thickness (m)</td>
<td>(\zeta)</td>
</tr>
<tr>
<td>Photolytic loss of DOC(_2) to DOC(_1) ((\mu)M DOC d(^{-1}))</td>
<td>(X_2)</td>
</tr>
</tbody>
</table>

\(^a\) Boyd et al. (1995)  
\(^b\) Walsh et al. (2001)  
\(^c\) Verity et al. (1991)  
\(^d\) Fortier et al. (1994)  
\(^e\) Nuthig and Bodungen (1989)
This $K_v$ value for nitrate is similar to that of 1.0 μM reported by Sommer (1986) for diatoms in the Drake Passage. The $K_v = 0.17$ μM value for ammonium uptake falls within the 0.04- 0.33 μM range reported by Cochlan and Bronk (2001) from the Ross Sea. Ammonium suppression of nitrate uptake was ignored in this model. Although no studies of ammonium- nitrate uptake interactions have been made along the West Antarctic Peninsula, Cochlan and Bronk (2001) found evidence for possible repression of nitrate uptake by elevated ammonium concentrations in the Ross Sea only at one site (of eight). Also, micronutrient limitation was not considered in the model. Moline and Prezelin (1996) suggested that in the near shore areas, i.e. Marguerite Bay, land sources of micronutrients such as Fe, which limits nitrate uptake by phytoplankton, might be sufficient for phytoplankton.

The fifth and the sixth terms in the Eq. (1) are phytoplankton losses. $\psi_j$, $\varepsilon_j$, $\gamma_j$, and $\eta_j$ are the rates of phytoplankton biomass loss due to excretion of DOC$_1$, respiration, grazing, and cell lysis, respectively, and $w_j$ is sinking velocity (Table 10). Algal respiration is usually either ignored or considered to be insignificant relative to heterotrophic respiration (Geider, 1998). However, Dickson and Orchard (2001) showed that oxygen consumption by phytoplankton can be a significant sink (up to 60% of net community respiration) for gross production. Respiration of diatoms at the daily rate of 1% of their net biomass was established with the preliminary model runs. The more shade adapted cryptophytes and prymnesiophytes had smaller respiration rates of 0.5%.

With regard to phytoplankton loss due to their excretion of dissolved compounds ($\psi_j$), Moran and Estrada (2002) reported DOC release of 13% of primary production for the region dominated by large diatoms and 17% for that dominated by Cryptophyceae in
the Gerlache Strait (WAP) area. Ducklow et al. (2000) estimated DOC release must be 6-20% of gross primary production to meet bacterial carbon requirements in the Ross Sea. Prymnesiophytes usually have higher excretion rates than diatoms and cryptophytes (Schoemann et al., 2005), ranging from <5 to >50% (Nagata, 2000—cited in Ducklow et al., 2000). The model’s excretion of monomeric DOM was set at the rates of 10% of primary production for diatoms and cryptophytes and 40% of primary production for prymnesiophytes. Additional phytoplankton loss to the macromolecular DOM pool due to autolysis of phytoplankton cells was assumed to be 1% of biomass of each phytoplankton group to account for bacterial remineralization of non-living macromolecular organic matter of phytoplanktonic origin.

Both diatoms and prymnesiophytes had non-linear settling velocities, \( w_J \) in Eq. (1), to allow for aggregations, which sink at a greater rate than single-cell phytoplankton. The cryptophytes instead had a small linear sinking rate of 0.025 m d\(^{-1}\) in the model (Table 10). The sinking velocities used in this model (Table 10) were significantly lower than those in Walsh et al. (2001) to allow for accumulation of high phytoplankton stocks, \(~20 \text{ mg chl } a \text{ m}^{-3}\) within the euphotic zone, typically observed in Marguerite Bay (Karl et al., 1992; Garibotti et al., 2003a, b). With diatom sinking rate of 0.001*\( P^2 \) m d\(^{-1}\) and diatom biomass of 20 mg chl \( a \) m\(^{-3}\), particulate carbon flux would be approximately 320 mg C m\(^{-2}\) d\(^{-1}\) (26.8 mmol C m\(^{-2}\) d\(^{-1}\)), which falls within the ranges of 115-800 mg C m\(^{-2}\) d\(^{-1}\) reported by Anadon et al. (2002) and of 3.0-31.1 mmol C m\(^{-2}\) d\(^{-1}\) observed by Karl et al. (1991) for the northeastern Bellingshausen Sea.
4.2.4.2. **Zooplankton: grazing and excretion**

The most abundant macro- and mesozooplankton found in the waters of the Antarctic Peninsula are Antarctic krill *Euphausia superba*, copepods, and salps.

Crustaceans are known to be selective filter feeders that feed mostly on large size plankton (>20 μm) such as diatoms. They also may feed on large protozoa, and, in the periods of low food abundance, on other crustaceans. Smaller phytoplankton therefore were considered to be subjects of protozoan grazing only. Since no salps were found during summer and autumn surveys of Marguerite Bay, they were neglected in the model.

Crustacea grazing stress on diatoms (γPₐ) was governed by prey availability above a grazing threshold value (Table 10) and food demands of herbivore stocks. The grazing stress coefficient, γ, in Eq. (1) was therefore computed as a ratio of total daily zooplankton carbon demands (mg C m⁻² d⁻¹), or maximal grazing stress, to depth integrated diatom biomass (mg C m⁻²). If maximal crustacean grazing stress was greater than depth integrated diatom stocks, crustacean demands were not satisfied and they grazed on only as much prey as was available.

In the winter months, when prey stocks of diatoms are usually minimal (Prezelin et al., 2004) and close to the imposed grazing threshold, maximal crustacean grazing stress was set to a minimal value of 1 mg C m⁻² d⁻¹ (Table 11). Maximal grazing stress for summer and autumn months of 2000-2001 and 2001-2002 in Table 11 was computed using zooplankton abundance from field data (Ashjian et al., 2004; Ross and Quétin, 2001, 2002) and assumed zooplankton carbon demands derived from the following considerations. In autumns of 2001 and 2002, the carbon biomass of an adult krill ranged from 32 to 233 mg C (Kendra Daly, per. com.) and, since a krill’s carbon demands are
Table 11. Monthly average maximal grazing stress (mg C m\(^{-2}\) d\(^{-1}\)) on diatoms during the (a) 2000-2001 and (b) 2001-2002 modeled years.

<table>
<thead>
<tr>
<th></th>
<th>Aug</th>
<th>Sep</th>
<th>Oct</th>
<th>Nov</th>
<th>Dec</th>
<th>Jan</th>
<th>Feb</th>
<th>Mar</th>
<th>Apr</th>
<th>May</th>
<th>Jun</th>
<th>Jul</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) 2000-2001</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>2.0</td>
<td>32</td>
<td>200</td>
<td>300</td>
<td>600</td>
<td>800</td>
<td>840</td>
<td>400</td>
<td>2.0</td>
</tr>
<tr>
<td>Maximal grazing stress (mg C m(^{-2}) d(^{-1}))</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>2.0</td>
<td>32</td>
<td>250</td>
<td>400</td>
<td>300</td>
<td>250</td>
<td>250</td>
<td>250</td>
<td>2.0</td>
</tr>
<tr>
<td>b) 2001-2002</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>2.0</td>
<td>32</td>
<td>250</td>
<td>400</td>
<td>300</td>
<td>250</td>
<td>250</td>
<td>250</td>
<td>2.0</td>
</tr>
</tbody>
</table>
approximately 5% body carbon per day (Pakhomov et al., 1997), ingestion demand of an adult krill was assumed to be 5 mg C d$^{-1}$, which was in agreement with carbon incorporation rates estimated by Anadon et al. (2002). The daily food demand of a juvenile krill was assumed to be 2 mg C d$^{-1}$. The average carbon biomass of krill larvae was approximately 0.20 mg C in the autumn of 2001 (Daly, 2004; Pakhomov et al., 2004). Assuming a larval requirement of 20% body carbon, a krill larva might consume 0.04 mg C d$^{-1}$. Assuming further an average carbon biomass of small and large copepods of 0.05 and 0.1 mg C, respectively, (Conover and Huntley, 1991) and mesozooplankton daily carbon requirements of 5% of body carbon, they might ingest 0.0025 mg C d$^{-1}$ and 0.05 mg C d$^{-1}$, respectively. Grazing stress in the model was set at twice the ingestion demands of each krill stage and copepods to allow for sloppy feeding and the release of DOC$_2$.

In January 2001, krill abundance was ~15 ind. m$^{-2}$ (Ross and Quetin, 2001). Assuming that the krill population was composed of 5 adults and 10 juveniles, their grazing stress on diatoms would have been 50 mg C m$^{-2}$ d$^{-1}$ and 40 mg C m$^{-2}$ d$^{-1}$, respectively. Since no larval krill or copepod abundances were reported in January 2001, their abundances were taken to be half of those in the following autumn: 500 ind. m$^{-2}$ and 10,000 (small copepods) ind. m$^{-2}$, respectively (Ashjian et al., 2004). With krill larvae and copepod requirements given above they might have grazed 40 mg C m$^{-2}$ d$^{-1}$ and 50 mg C m$^{-2}$ d$^{-1}$, respectively. Total grazing stress on diatoms for January 2001 was estimated to be 200 mg C m$^{-2}$ d$^{-1}$ (Table 11).

During autumn of 2001 greater zooplankton stocks were observed: euphausiids – 60 ind. m$^{-2}$ (large euphausiids dominated – Ashjian et al., 2004) that required 600 mg C
m² d⁻¹; 1000 larval euphausiids (Ashjian et al., 2004) with 80 mg C m² d⁻¹ carbon requirements; and copepods – 20,000 ind. m² (12000 large and 8000 small – from Ashjian et al., 2004) that might have grazed 160 mg C m² d⁻¹. To sum up, total grazing stress on diatoms in autumn of 2001 was imposed as 840 mg C m⁻² d⁻¹ (Table 11).

Since there were no Marguerite Bay zooplankton data available for summer of 2001-2002, crustacean grazing stress was calculated using zooplankton stocks observed at the entrance to Marguerite Bay (Fig. 37) during LTER January 2002 survey. Assuming that the krill population of 40-80 ind. m² (Ross and Quentin, 2002) consisted of juveniles, their grazing stress would have been 160-320 mg C m² d⁻¹. Abundance of larval euphausiids and copepods in summer of 2002 was assumed to be the same as in summer of 2001. Total grazing stress was set to be maximal in February – 400 mg C m² d⁻¹ (Table 11).

Yet, the crustacean stocks in autumn of 2002 were considerably lower than those in autumn of 2001. Those were ~20 ind. m² of euphausiids, ~45 ind. m² of larval euphausiids, 10,000 ind. m² of small copepods and 3,600 ind. m² of large copepods (Ashjian, per.comm.). Total grazing stress on diatoms was imposed as 250 mg C m² d⁻¹ in autumn of 2002 (Table 11).

35 % of the model’s zooplankton ingestion flux was converted to fecal pellets. The temporal dynamics of fecal pellets of each crustacean group, Zᵢ, was governed by the following equation:

\[ \frac{\partial Z_i}{\partial t} = \frac{\partial}{\partial x} K_x \frac{\partial}{\partial x} Z_i + \frac{\partial}{\partial z} K_z \frac{\partial}{\partial z} Z_i + \rho_i (1-\xi_i) \gamma_i [P_i] + X_3 - \frac{\partial}{\partial z} w_i Z_i - \tau_i Z_i \]

\[ (5) \]
In the third term of Eq. (5) \( \rho_f \) is a fraction of ingested phytoplankton that is released as fecal pellets, \( \gamma_f [P_f] \) – grazed phytoplankton stocks, \( \xi_f \) – losses of grazed phytoplankton due to sloppy feeding. The fourth term, \( X_3 \), is additional source of pellets from consumption of protozoans by adult krill. Fecal pellet losses in Eq. (5) include sinking (the fifth term) and pellet lysis, \( \tau_f \) (the sixth term). The last term accounts for degradation of pellets by meso- and macrozooplankton (coprophagy and coprohexy) (Gonzales and Smetacek, 1994) and prokaryotic pellet dissolution (Cho and Azam, 1988; Goeyens et al., 1991). It was assumed that pellet lysis may somewhat diminish the downward flux of this organic matter despite high pellet sinking rates (Table 10).

Since zooplankton biomass was not converted to biomass of their predators in the model, the remaining 65% of ingested material was respired and excreted as DIC and NH\(_4\). Huntley and Nordhausen (1995) and Atkinson and Whitehouse (2001) found ammonium excretion rates of 3-9 \( \mu \)mol N g\(^{-1}\) dry wt h\(^{-1}\) for Antarctic crustacean zooplankton. Assuming the average C/dry wt ratio of 0.45 (C/dry wt ratio ranged from 0.36 to 0.56 during the measurements of Huntley and Nordhausen (1995) and Atkinson and Whitehouse (2001)) and the Redfield C: N ratio of 6.6 for zooplankton, those ammonium excretion rates convert to metabolic losses of body carbon of 1-4 % C d\(^{-1}\). Using the assumption of crustacean daily ingestion rate of 5% body carbon, this translates to excretion and respiration losses of 20-80% of ingested biomass.

4.2.4.3. Protozoan dynamics

The antarctic microzooplankton community is dominated by protozoan organisms, ciliates and heterotrophic flagellates (Karl et al., 1996). They feed mostly on small phytoplankton (<20 um) and bacteria. Microzooplankton abundance can vary by
more than three orders of magnitude from winter to summer in Antarctic waters (Caron et al., 2000) and is often positively correlated with phytoplankton biomass (Burkill et al., 1995; Caron et al., 2000). Alder and Boltovskoy (1991) found total microzooplankton biomass to be >10 mg C m\(^{-3}\) in Marguerite Bay during summer 1989. With protozoan ingestion demands being as high as 50% of body carbon per day (Burkill et al., 1995), grazing rate by protozoans was considered to be proportional to cryptophyte and prymnesiophyte concentrations (i.e. \(= \gamma_p P \))}, where the specific protozoan grazing coefficient \(\gamma_p\) was 0.125 (mg chl a m\(^{-3}\) d\(^{-1}\)) after Burkill et al. (1995). 40% of the organic matter ingested by protozoans was released as fecal pellets which underwent the same dynamics as those of crustaceans. Protozoans can be a significant source of ammonium (Goeyens et al., 1991) with a protozoan ammonium regeneration rate in a proportion to protozoan carbon biomass of as much as \(\sim 2.6 \mu\text{mol} \text{ (NH}_4\text{)} (\text{mg} \text{ C})^{-1} \text{ d}^{-1}\). In the model, 50% of POM ingested by protozoans was lost to DIC and NH\(_4\). Additional protozoan transfer of POM to DIC and NH\(_4\) occurred through grazing on bacteria and was included into bacteria mortality rate.

4.2.4.4. Microbial loop dynamics

Remineralization of organic matter in the model was performed by two groups of bacteria, the ammonifiers, \(B\), and the nitrifiers (Table 10). Of these, the former are a state variable, \(B\), while the latter are a constant flux term, \(X_1\). Two pools of organic matter, monomolecular DOC\(_1\) and macromolecular DOC\(_2\), are directly available to the ammonifying bacteria in the model:

\[
\frac{\partial}{\partial t} B = \frac{\partial}{\partial z} Kz \frac{\partial}{\partial z} B + \frac{\partial}{\partial x} Kx \frac{\partial}{\partial x} B + (1-\beta) v_{\text{DOC1}} B + (1-\beta) v_{\text{DOC2}} B \\
- m B,
\]

(6)
The third and the forth terms of the Eq. (6) are bacterial growth terms, expressed as uptake of DOC. Monomeric DOC$_1$ was the primary substrate for ammonifying bacteria. Bacteria utilized DOC$_2$ only when their organic matter requirements were not satisfied by DOC$_1$. A possible role of bacteria in remineralization of particulate organic matter was implied in the breakdown of both zooplankton pellets as the pellet lysis term $\tau$ of Eq. (5) and phytoplankton debris as the phytoplankton autolysis tem $\eta$ of Eq. (1). Both POM sources yielded macromolecular DOC$_2$, which later become available to bacterial uptake. Rates of DOC$_1$ and DOC$_2$ uptake were:

$$v_{\text{DOC}_1} = \mu_B \left[ \text{DOC}_1 (K_{\text{SDOC}} + \text{DOC}_1)^{-1} \right]$$

$$v_{\text{DOC}_2} = \mu_B \chi \left[ \text{DOC}_2 (K_{\text{SDOC}} + \text{DOC}_2)^{-1} \right]$$

A wide range of bacterial growth rates was reported for the Southern Ocean: bacterial doubling times were as long as 14-45 days (Pedros-Alio et al., 2002) and 5-70 days (Lochte et al., 1996), and as short as 1.25 days (Tupas et al., 1994) and 1.28 days (Bird and Karl, 1990). Considering inhibitory effects of Antarctic low temperatures (<3°C) on bacterial metabolism (Pomeroy and Deibel, 1986), maximal growth rate for bacteria, $\mu_B$ in Eq. (7) of the model, was 0.32 d$^{-1}$.

Since extracellular enzymes must be released by bacteria to hydrolyze macromolecular DOC$_2$, only 80% of DOC$_2$, $\chi$ in Eq. (7b), was consumed by bacteria. Moreover, only a fraction of the assimilated DOC, (1-$\beta$), was converted into bacterial biomass. The assumed 35% conversion efficiency was in agreement with 30% efficiency reported from Atlantic sector of the Southern Ocean by Kahler et al. (1996) and 35-45% efficiency range estimated by Ducklow et al. (2000) for the Ross Sea. The remaining 65% of the assimilated DOC was regenerated as DIC and NH$_4$. Although bacteria can
take up ammonium from the surrounding waters to satisfy their nitrogen requirements, the ammonification was higher than ammonium consumption in the Antarctic coastal waters (Tupas et al., 1994, Goeyens et al., 1991). Thus, the model assumed that nitrogen demands of the ammonifiers in surface waters were met by the uptake of DOM. The last term of Eq. (6), bacterial mortality – m B, incorporated bacterial losses due to protozoan grazing (Bird and Karl, 1990) and viral lysis (Guixa-Boixereu et al., 2002).

When uptake by bacteria was the sink for monomolecular DOC$_1$, the DOC$_1$ sources included both excretion from phytoplankton, $\psi_j$, and photolysis of macromolecular DOC$_2$, $X_2$, in the surface waters:

$$\frac{\partial}{\partial t} \text{DOC}_1 = \frac{\partial}{\partial x} Kx \frac{\partial}{\partial x} \text{DOC}_1 + \frac{\partial}{\partial z} Kz \frac{\partial}{\partial z} \text{DOC}_1 - v_{\text{DOC}_1} B + \sum_j \psi_j P_j + X_2$$  \hspace{1cm} (8)

Photolytic decay of DOC$_2$ was a constant (Table 10) and occurred at day time within the upper 5 meters of the water column. Macromolecular DOC$_2$, in turn, was derived from zooplankton sloppy feeding, $\xi_1$ and dissolution of zooplankton pellets, $\tau_1$, and phytoplankton debris, $\eta_1$:

$$\frac{\partial}{\partial t} \text{DOC}_2 = \frac{\partial}{\partial z} Kz \frac{\partial}{\partial z} \text{DOC}_2 + \frac{\partial}{\partial x} Kx \frac{\partial}{\partial x} \text{DOC}_2 - v_{\text{DOC}_2} B - X_2 + \sum_1 \sum_j \xi_j \gamma_j P_j + \sum_1 \tau_1 Z_1 + \sum_1 \eta_1 P_j$$ \hspace{1cm} (9)

4.2.4.5. **Dissolved inorganic pool**

As a state variable, total dissolved inorganic carbon (DIC) underwent the following dynamics:

$$\frac{\partial}{\partial t} \text{DIC} = \frac{\partial}{\partial z} Kz \frac{\partial}{\partial z} \text{DIC} + \frac{\partial}{\partial x} Kx \frac{\partial}{\partial x} \text{DIC} - \sum_j v_j \text{NH}_4 P_j - \sum_j v_j \text{NO}_3 P_j + \sum_j \epsilon_j P_j + \sum_1 \delta_1 (1 - \xi_j) \gamma_1 P_1 + (\beta + m) B$$ \hspace{1cm} (10)
The seasonal changes of DIC were affected by the uptake of both dissolved CO$_2^{(aq)}$ and HCO$_3^-$ by phytoplankton during photosynthesis, by the respiration of phytoplankton, zooplankton, and bacteria, by lateral and vertical exchange. Since CO$_2$ is a gas, exchange across sea-surface interface was also considered (Walsh and Dieterle, 1995). The nitrate stocks were impacted by uptake by phytoplankton, which can potentially reduce nitrate concentration to zero in Marguerite Bay (see Chapter 1), by oxidation of ammonium by nitrifying bacteria, $X_1$, and by mixing with deep and offshore waters:

$$\frac{\partial \text{NO}_3}{\partial t} = \frac{\partial}{\partial z} \text{Kz} \frac{\partial}{\partial z} \text{NO}_3 + \frac{\partial}{\partial x} \text{Kx} \frac{\partial}{\partial x} \text{NO}_3 - 0.15 \sum \omega_j \text{NO}_3 P_j$$

+ $X_1$,  \hspace{1cm} (11)

where 0.15 is an inverse Redfield C: N ratio for phytoplankton. In this model, nitrifying bacteria are not a state variable. Instead, nitrification ($X_1$) is assumed to occur at a constant rate of 0.02 $\mu$M d$^{-1}$ (Table 10) which was determined during preliminary model runs, at PAR, $I(z)$, <0.01 of $I(\theta)$, i.e. at night and within the aphotic zone.

Finally, ammonium dynamics was described by:

$$\frac{\partial \text{NH}_4}{\partial t} = \frac{\partial}{\partial z} \text{Kz} \frac{\partial}{\partial z} \text{NH}_4 + \frac{\partial}{\partial x} \text{Kx} \frac{\partial}{\partial x} \text{NH}_4 - 0.15 \sum \omega_j \text{NH}_4 P_j$$

- $X_1 + 0.15 \sum \delta_1 (1 - \xi_1) \gamma_1 P_1 + 0.20 (\beta+m) B$  \hspace{1cm} (12)

The third and the fourth terms of Eq. (12) reflect ammonium consumption by phytoplankton and nitrifying bacteria. The sixth term was a source of ammonium through excretion by all three groups of zooplankton. The seventh term was ammonium production through bacterial ammonification and mortality. A different N: C ratio of 0.20 was used for bacteria.
4.2.5. Model implementation

Effects of light limitation imposed by sea ice and zooplankton grazing pressure on Marguerite Bay plankton community and nutrient cycling were studied with two model scenarios. The first scenario was based on the physical conditions, including sea ice concentration, mixed-layer temperature, mixed-layer salinity, mixed-layer depth, surface wind stress (Table 8a), and grazing stress of zooplankton (Table 11a) observed during 2000-2001 in Marguerite Bay. The second scenario included the physical conditions (Table 8b) and zooplankton grazing pressure (Table 11b) observed in the bay during 2001-2002. Although the scenarios’ conditions were different, the equations for the state variables described in the previous section were solved using the same parameterization (Table 10) and the same initial and boundary conditions (Table 9) for both scenarios. The goal, thus, was to evaluate whether the difference in the conditions indeed caused the observed changes, namely, the reduction of NCP and ammonium stocks (Table 7) between two years.

Next, the second goal of the modeling experiment – whether bacterial ammonification or zooplankton excretion were the primary sources of high ammonium stocks in Marguerite Bay – was approached with the following experimental runs. First, zooplankton grazing pressure was changed from high to low for the first year scenario and from low to high for the second year scenario to evaluate the importance of zooplankton excretion on ammonium production. Second, the importance of ammonifying bacteria in build up of ammonium pool was assessed by increasing and decreasing bacterial production for both scenarios.
Finally, a number of the model parameters in Table 10 were either not supported by the field observations and were decided upon during the preliminary model runs or chosen from a wide range of reported values. Thus, a sensitivity analysis was performed to check how strongly the model results depend on uncertain parameterization.

4.3. **Modeling results**

4.3.1. *Time evolution of nitrate and ammonium in Marguerite Bay in 2000-2001 and 2001-2002 seasons*

The model’s nutrient fields should be representative of the Marguerite Bay observations if the model is a reliable tool for studying biogeochemical cycles in the bay. The simulated 2000-2001 and 2001-2002 seasons were started on 25 August, when the observed nitrate concentrations, $\sim 28 \mu M$, were not yet at their seasonal maxima. The model’s maximal mixed-layer nitrate concentrations of $>30 \mu M$ were reached by October of each year (Figs. 41a, c) after vertical and lateral exchange of high-nitrate deep and offshore waters as well as local oxidation of ammonium to nitrate by nitrifying bacteria.

The rapid development of model’s summer bloom during the model’s December of 2000 resulted in significant depletion of nitrate in the surface waters with nitrate concentrations being $<1 \mu M$ within the upper 10 m by the end of January (Fig. 41a). This is in agreement with observations made during the LTER survey to Marguerite Bay during January 2001 (Fig. 42a).

Fig. 43a shows that nitrate was a primary nitrogen source for Marguerite Bay phytoplankton ($f$-ratio $>0.8$) during the first summer months of the 2000-2001 season.

The concentration of another nitrogenous nutrient, ammonium, decreased from its initial value of $\sim 1.0 \mu M$ in August of 2000 to $<0.05 \mu M$ in the spring months (Fig. 41b).
Fig. 41. The model’s annual cycles of (a) nitrate (μM) and (b) ammonium (μM) during 2000-2001 scenario and (c) nitrate (μM) and (d) ammonium (μM) during 2001-2002 scenario in Marguerite Bay.
Fig. 42. (a) Vertical profile of nitrate concentration (µM) at a LTER station in Marguerite Bay (see Fig. 1a for location) during January 2001. (b) Average profile (solid line) of nitrate concentration (µM) in Marguerite Bay during April-May 2001. Dashed lines indicate standard deviation envelope. (c) Average profile (solid line) of nitrate concentration (µM) in Marguerite Bay at the end of July 2001. (d) Profile of nitrate concentration (µM) at a LTER station at the entrance to Marguerite Bay (see Fig. 1e for location) during January 2002. (e) Average profile (solid line) of nitrate concentration (µM) in Marguerite Bay during April-May 2002.
Fig. 43. Simulated time series of total DIN, nitrate, and ammonium uptake by phytoplankton (mmol N m$^{-2}$ d$^{-1}$) in Marguerite Bay for (a) 2000-2001 and (b) 2001-2002 model scenarios.

Apparently, uptake by phytoplankton kept ammonium concentrations low, <0.5 µM, in the upper 20 m of the water column during the summer of 2001. Yet ammonium production by heterotrophs and bacteria resulted in the formation of ammonium subsurface maximum, 1.5 -2 µM, below the euphotic zone in late January-February (Fig. 41b), in agreement with the field observations (Fig. 44a). With increasing stocks of ammonium from late summer into autumn (Fig. 41b) the net uptake of ammonium by phytoplankton also increased (Fig. 43a) bringing the f-ratio to 0.50 by the end of the bloom. Despite increased ammonium uptake in the autumn, the model’s ammonium concentrations continued to increase, reaching the values of 4-5 µM during the model’s April-May 2001 (Fig. 41b). Similar values for ammonium concentration were observed during SO GLOBEC survey to Marguerite Bay in April-May 2001 (Fig. 44b). Note that the simulated ammonium concentration of ~1.9 µM matched well the observed ones within the surface mixed-layer at the end of July (Figs. 41b and 44c). Furthermore, the
Figure 44. (a) Vertical profile of ammonium concentration (μM) at a LTER station in Marguerite Bay (see Fig. 1a for location) during January 2001. (b) Average profile (solid line) of ammonium concentration (μM) in Marguerite Bay during April-May 2001. Dashed lines indicate standard deviation envelope. (c) Average profile (solid line) of ammonium concentration (μM) in Marguerite Bay at the end of July 2001. (d) A profile of ammonium concentration (μM) at a LTER station at the entrance to Marguerite Bay (see Fig. 1e for location) during January 2002. (e) Average profile (solid line) of ammonium concentration (μM) in Marguerite Bay during April-May 2002.
simulated nitrate concentrations during April-May (17-20 μM) and July (~27 μM) 2001 replicated the corresponding observed values (Fig. 41a, 42c).

During the 2001-2002 model scenario, a seasonal reduction of near-surface nitrate concentrations from ~30 μM in November of 2001 to ~4 μM in February of 2002 occurred (Fig. 41c). There are no field data for Marguerite Bay for summer of 2002, yet a profile of nitrate concentration for the most shoreward station of line 200 in January of 2002 (see Fig. 1e for the location) is in agreement with the corresponding model results (Fig. 42d). Ammonium concentrations at the same station reached ~2 μM at approximately 20 m depth in January 2002 (Fig. 44d). The simulated ammonium concentration maximum was ~0.5-1.5 μM during model’s January-February 2002 (Fig. 41d). The simulated mixed-layer nitrate (Fig. 41c) and ammonium (Fig. 41d) concentration values of 15-20 μM and 1.6-2.8 μM, respectively, for model’s April-May 2002 also compared well to the corresponding field observations (Fig. 42e and 44e).

There was a considerable difference in the amount and the length of the period of maximal nitrate drawdown between these two years. In 2000-2001, the simulated nitrate concentrations within the top 10 m were reduced essentially to zero from January to late February (Fig. 41a). During the 2001-2002 model scenario, nitrate concentrations within the upper water column were reduced to only ~4 μM, while the period of maximal nitrate depletion lasted only one month (Fig. 41c). Fig. 42b shows that, although the magnitude of the maximal DIN uptake during the 2001-2002 was the same as during 2000-2001 the period of elevated DIN uptake in 2001-2002 was shorter than that in 2000-2001. As a result, primary production computed as integrated total DIN uptake over the 2001-2002 growing season (1.9 mol m⁻²) was less than that in 2000-2001 (2.5 mol m⁻²).
4.3.2. *Phytoplankton stocks dynamics in Marguerite Bay for the 2000-2001 and 2001-2002 model scenarios*

The simulated changes of chlorophyll as a function of time over the 2000-2001 and 2001-2002 are shown in Figs. 45a and 46a, respectively. In both years the modeled chlorophyll concentrations reached 17-20 mg m$^{-3}$. They matched the observed maxima of pigment values (Figs. 27 and 29) and are typical for Marguerite Bay (Karl et al., 1992; Garibotti et al., 2003a, b, 2005). Yet, the model’s phytoplankton biomass reached $>$17.5 mg chl $a$ m$^{-3}$ by the end of December persisting until March during the first year (Fig. 45a). On the other hand, chlorophyll concentrations reached their maxima of $\sim$17 mg m$^{-3}$ only by the end of February and lasted for just one month during the second year (Fig. 46a). This difference in the timing of the bloom between the two years was consistent with greater depletion of nitrate in the first year (Fig. 41a), compared to that in the second (Fig. 41c).

In terms of phytoplankton community structure, the diatoms generally dominated during both modeled years (Figs. 45 and 46). Diatoms accounted for 95% of chlorophyll biomass during the blooms and for 75% (2000-2001) and 65% (2001-2002) of integrated annual primary production (Figs 47 and 48). This was consistent with conclusions made from examination of Def (TIN): Def (PO$_4$) and Def (SIL): Def (TIN) ratios in Chapter 1. Cryptophytes dominated the model’s phytoplankton community only at the early stages of the bloom in both years. However, their biomass did not exceed 1.5 mg chl $a$ m$^{-3}$ (Figs. 45c and 46c).

Concentrations of the other phytoplankton group of this model, prymnesiophytes, were also low in both years at $<$1 mg chl $a$ m$^{-3}$ (Figs. 45d and 46d).
(a) Total Chlorophyll $a$ [mg (chl $a$) m$^{-3}$]  
(b) Diatoms [mg (chl $a$) m$^{-3}$]

![Graph](image1)

(c) Cryptophytes [mg (chl $a$) m$^{-3}$]  
(d) Prymnesiophytes [mg (chl $a$) m$^{-3}$]

![Graph](image2)

Fig. 45. The model’s annual cycles of biomass (mg chl $a$ m$^{-3}$) of (a) total chlorophyll, (b) diatoms, (c) cryptophytes, and (d) prymnesiophytes in Marguerite Bay for the 2000-2001 scenario.

(a) Total chlorophyll $a$ [mg (chl $a$) m$^{-3}$]  
(b) Diatoms [mg (chl $a$) m$^{-3}$]

![Graph](image3)

(c) Cryptophytes [mg (chl $a$) m$^{-3}$]  
(d) Prymnesiophytes [mg (chl $a$) m$^{-3}$]

![Graph](image4)

Fig. 46. The model’s annual cycles of biomass (mg chl $a$ m$^{-3}$) of (a) total chlorophyll, (b) diatoms, (c) cryptophytes, and (d) prymnesiophytes in Marguerite Bay for the 2001-2002 scenario.
Fig. 47. Simulated net primary production (g C m\(^{-2}\) d\(^{-1}\)) and grazing losses (g C m\(^{-2}\) d\(^{-1}\)) of (a) diatoms, (b) cryptophytes, and (c) prymnesiophytes in Marguerite Bay during 2000-2001.

Fig. 48. Simulated net primary production (g C m\(^{-2}\) d\(^{-1}\)) and grazing losses (g C m\(^{-2}\) d\(^{-1}\)) of (a) diatoms, (b) cryptophytes, and (c) prymnesiophytes in Marguerite Bay during 2001-2002.

Model’s cryptophyte biomass was largely controlled by microzooplankton grazing, while prymnesiophyte production was limited by losses to the DOC pool via excretion of DOC\(_1\) and lysis. On average, 60% of prymnesiophyte production was lost to DOC pool in the model, in agreement with the values reported by Schoemann et al. (2005). The effect of variability of excretion losses on prymnesiophyte biomass and primary production is illustrated in Fig. 49a. With the fraction of growth excreted as DOC\(_1\), \(\psi\), being 0.40, as used in the model (Table 10), prymnesiophyte biomass was <1 mg chl \(a\) m\(^{-3}\) and they contributed to 9% and 18% of the model’s total annual primary production in 2000-2001 and 2001-2002, respectively. Perturbation of \(\psi\) resulted in more
than a magnitude variability of prymnesiophyte biomass from <0.1 mg chl $a \ m^{-3}$ at $\psi=0.60$ to 2-2.5 mg chl $a \ m^{-3}$ at $\psi=0.10$ (Fig. 49a). Correspondingly, prymnesiophyte fraction of total annual primary production varied from as low as 1% to as high as 75% at $\psi=0.10$ for the 2001-2002 scenario.

Fig. 49. (a) The model response of prymnesiophyte biomass (mg chl $a \ m^{-3}$) to perturbation of prymnesiophyte fraction of growth excreted as DOC$_1$, $\psi$; the percentage of the annual prymnesiophyte production of the total annual primary production. (b) The model response of cryptophyte biomass (mg chl $a \ m^{-3}$) to perturbation of grazing rate coefficient $\gamma_p$; the percentage of the annual cryptophyte production of the total annual primary production.

Similarly, since on average nearly 70% of cryptophyte production was grazed in the model, variability in microzooplankton grazing pressure specified by grazing rate coefficient, $\gamma_p$ (Table 10), resulted in changes of cryptophyte biomass from 1 mg chl $a \ m^{-3}$ at $\gamma_p$ being twice larger than the value in Table 10 to 10 mg chl $a \ m^{-3}$ for a four-fold reduced $\gamma_p$ value (Fig. 49b). However, cryptophyte populations of > 4 mg chl $a \ m^{-3}$ are rarely developed in the Antarctic waters (Rodriguez et al., 2002; Garibotti et al., 2005).
Apparently, large microzooplankton grazing pressure keeps small-size phytoplankton from blooming in the Southern Ocean (Pondaven et al., 2000). Thus, uncoupling cryptophytes and their grazers was not considered as a possible scenario for the model.

Overall, with 70% of cryptophyte production and 23% of prymnesiophyte production being grazed in the model (Figs. 47b, c and 48b, c), required microzooplankton stocks were supported during both modeled years. Assuming microzooplankton food demands of 50% of body carbon, such modeled grazing pressure sustained protozoan biomass of ~1.3 g C m⁻² (2000-2001) and ~0.75 g C m⁻² (2001-2002) that compared well to the Marguerite Bay observations of Alder and Bolstovsky (1991).

Grazing losses of diatoms were moderate and were specified by zooplankton stocks from the field observations (Table 11). They amounted to 10-25% of diatom net primary production during summer months of 2000-2001 and 2001-2002 (Figs. 47a and 48a). Yet 100% of net diatom production was lost to zooplankton by April 2001. Zooplankton stocks were lower in autumn of 2002 than in autumn of 2001 and thus consumed only 30-50% of net autumnal diatom production (Fig. 48a).

4.3.3. **Simulated dissolved organic carbon and bacterial dynamics in Marguerite Bay during the 2000-2001 and 2001-2002 seasons**

These simulated 2000-2001 and 2001-2002 blooms of high phytoplankton biomass were immediately followed by formation of large pools of dissolved organic matter in the model. There were no measurements of DOM for Marguerite Bay. Yet, there have been a few DOM observations from similar Antarctic coastal regions of the Ross Sea and Gerlache Strait. Just like Marguerite Bay, these regions were characterized by high summer diatom production (Sweeney et al., 2000a, b; Varela et al., 2002) and
large depletions of nutrients in the surface waters. High ammonium concentrations and stocks were also observed in those regions (Gordon et al., 2000; Bode et al., 2002).

Carlson et al. (2000) measured DOC values of up to 30 μM in excess over the background refractory DOC values during summer 1997 in the Ross Sea. Doval et al. (2002) reported 10-60 μM for the excess DOC concentrations in Gerlache Strait (WAP) during summer of 1995-1996, with the highest DOC values typically co-located with the highest chlorophyll a concentrations.

The model’s DOC concentrations in Marguerite Bay matched the values reported for those Antarctic coastal areas. In 2000-2001 scenario, concentrations of total DOC (sum of monomeric DOC and macromolecular DOC) reached their maximum of ~50 μM in model’s January (Fig. 50a). During the second modeled year, DOC concentrations were < 30 μM, somewhat lower than in the first year (Fig. 50c). In the model, DOC was derived from excretion by phytoplankton during photosynthesis, autolysis of dead phytoplankton cells, sloppy feeding of crustaceans, and lysis of zooplankton fecal pellets. In both modeled years, generally 40-50 % of DOC was supplied through lysis, primarily of phytoplankton debris. Additional 20-40 % of DOC was produced through phytoplanktonic excretion of dissolved organic compounds. Thus, phytoplankton were the primary DOC source in the Marguerite Bay model. Since stocks of phytoplankton diminished from one year to the next, the smaller amount of DOC was produced in the second year.

The DOC fueled bacterial production, which reached maxima during March-April of both modeled years (Figs 50b, d). A time lag between the peak of the phytoplankton bloom and maximal bacterial secondary production was apparent. In 2000-2001, maximal
Fig. 50. The model’s Marguerite Bay annual cycles of (a) dissolved organic carbon (DOC$_1$+DOC$_2$) (µM) and (b) bacterial biomass (mg C m$^{-3}$) for 2000-2001 model scenario and (c) total labile dissolved organic carbon (DOC) (µM) and (d) bacterial biomass (mg C m$^{-3}$) for 2001-2002 model scenario.

bacterial biomass of $\sim$5.6 mg C m$^{-3}$ was reached by the end of March (Fig. 50b), approximately a month after the peak of phytoplankton bloom in February (Fig. 45a). Similarly in 2001-2002, the bacterial maximum of $\sim$2.6 mg C m$^{-3}$ (Fig. 50d) during March-April occurred a month after the peak of the phytoplankton bloom in late February (Fig. 46a). A delay in bacterial response to phytoplankton production has been previously reported for the Antarctic waters (Bird and Karl, 1991; Clarke and Leakey, 1996; Moran and Estrada, 2002).

The values for bacterial biomass simulated in the model were slightly higher than those of 0.5-2 mg C m$^{-3}$ typically reported for some of the southern Antarctic waters (Lochte et al., 1996; Pedros-Alio et al., 2002). Yet, the values for maximal bacterial
biomass simulated in the model agreed well with the bacterial biomass values of 5-8 mg C m⁻³ reported by Clarke and Leakey (1996) for the northern tip of Antarctic Peninsula. Indeed, bacteria stocks as high as 24 mg C m⁻³ have been reported by Karl et al. (1991) for the WAP area.

4.3.4. *Ammonium production in Marguerite Bay during the 2000-2001 and 2001-2002 model runs*

The major differences between two scenarios were the concentration of sea ice and zooplankton grazing stress. The former being greater during the second year (Table 8, Figs. 31, 32) was likely to limit phytoplankton production during the 2001-2002 growing season. This effect, I hypothesize, should have lowered regeneration of ammonium in 2001-2002 compared to 2000-2001. However, greater autumnal zooplankton grazing during the first study year (Table 11), in turn, might have led to greater ammonium production due to greater zooplankton excretion during 2000-2001 compared to 2001-2002. Thus, one of the major goals addressed by the modeling was the identification of the principal producers of ammonium in the Marguerite Bay waters. Following the model’s state equations, ammonium could have been produced during bacterial respiration, excretion by herbivorous zooplankton, and sloppy microzooplankton feeding on bacteria. Figure 51 shows the simulated time-series of water column ammonium production during 2000- 2001 and 2001-2002.

In 2000-2001, simulated ammonium production increased from 1.5 mmol NH₄ m⁻² d⁻¹ during winter months to a maximum of 13.8 mmol NH₄ m⁻² d⁻¹ during April. Of all sources, the largest one was from the ammonifying bacteria, with ~45% of all ammonium produced during February-May 2001 (Fig. 51a). This result was in agreement with Tupas
et al. (1994), who found that bacteria regenerated 27-55% of total ammonium present in surface waters.

Figure 51. The simulated time series of ammonium production by zooplankton, microzooplankton, and bacteria (mmol NH$_4$ m$^{-2}$ d$^{-1}$) in Marguerite Bay for (a) 2000-2001 and (b) 2001-2002 scenarios.

The largest contribution from herbivorous zooplankton occurred at the beginning of the growing season (December), when it accounted for ~60% of ammonium production. Herbivorous zooplankton provided on average ~20% of ammonium from January to May 2001. Inputs of ammonium from bacteria mortality caused by both microzooplankton grazing and, possibly, viral lysis accounted for 30-40% of ammonium being produced in the Marguerite Bay surface waters during the growing season. It amounted to 100% of the total ammonium production during winter months (Fig. 51a). However, with low abundance of phytoplankton prey and absence of DOC as a substrate for bacteria, the production of ammonium from zooplankton excretion and bacterial ammonification appeared negligible during the Antarctic winter.

In 2001-2002, the maximal rate of ammonium production was ~8.0 mmol NH$_4$ m$^{-2}$ d$^{-1}$ from January to May (Fig. 51b). Overall, lower bacterial stocks in 2001-2002 led to
smaller ammonium production via bacterial ammonification and mortality than in 2000-2001. As in 2000-2001 herbivorous zooplankton provided up to 60% of ammonium during summer months of the 2001-2002 modeled year. However, reduction of crustacean stocks by autumn of 2002 reduced their ammonium production to 15% of the total ammonium production during April-May (Fig. 51b). Herbivore excretion of ammonium declined from ~3 mmol NH₄ m⁻² d⁻¹ during April 2001 (Fig. 51a) to ~1.2 mmol NH₄ m⁻² d⁻¹ in April 2002 (Fig. 51b).

These model results indicated that, despite a significant contribution of zooplankton to the ammonium pool, ammonifying bacteria were the primary source of ammonium in Marguerite Bay. To confirm this finding a sensitivity analysis of model’s ammonium field to changes in crustacean and bacterial biomass was performed (Table 12).

Table 12. Four cases of model’s responses in terms of ammonium concentration to changes of zooplankton and bacterial biomass.

<table>
<thead>
<tr>
<th>Scenario of physical conditions</th>
<th>Scenario of zooplankton grazing stress</th>
<th>Bacterial biomass (mg C m⁻³)</th>
<th>Maximal ammonium concentration (µM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 1</td>
<td>2001-2002</td>
<td>5.6</td>
<td>3.8</td>
</tr>
<tr>
<td>Case 2</td>
<td>2001-2002</td>
<td>2.6</td>
<td>3.3</td>
</tr>
<tr>
<td>Case 3</td>
<td>2000-2001</td>
<td>&lt;0.5</td>
<td>&lt;0.7</td>
</tr>
<tr>
<td>Case 4</td>
<td>2001-2002</td>
<td>&lt;0.4</td>
<td>&lt;0.5</td>
</tr>
</tbody>
</table>

Experimental case 1 was run with 2000-2001 physical conditions (Table 8a) and low autumnal 2001-2002 crustacean grazing stress of 200-250 mg C m⁻² d⁻¹ (Table 11b).
Just the opposite, case 2 had physical conditions of the 2001-2002 model scenario (Table 8b) and 2000-2001 autumnal grazing pressure of 800-840 mg C m$^{-2}$ d$^{-1}$ (Table 11a). Model cases 3 and 4 examined the effects of low bacterial biomass (Table 12). To achieve that maximal bacterial growth rate was reduced twice for the 2000-2001 and 2001-2002 model scenarios.

(a) Ammonium (μM) for 2000-01 scenario with 2001-02 zooplankton biomass

(b) Ammonium (μM) for 2001-02 scenario with 2000-01 zooplankton biomass

Figure 52. Simulated annual cycles of ammonium (μM) for (a) case 1 with 2000-2001 physical conditions (Table 8a) and 2001-2002 grazing stress (Table 11b) and (b) case 2 with 2001-2002 physical conditions (Table 8b) and 2000-2001 grazing stress (Table 11a).

The ammonium results of cases 1 and 2 are shown in Fig. 52. Indeed, the reduction of zooplankton biomass for the first year decreased maximal model’s ammonium concentration from 5.0 μM in the original scenario (Fig. 41b) to 3.8 μM (Fig. 52a). Yet, this value was still greater than the maximal 2001-2002 ammonium concentration of 2.8 μM (Fig. 39d). Similarly, the increase in zooplankton biomass for the 2001-2002 scenario brought maximal ammonium concentration only to 3.3 μM (Fig. 52b), still significantly lower than 5.0 μM of 2000-2001 scenario with the same grazing pressure. Hence, the 3.5-fold variability of zooplankton biomass caused 0.5-1.2 μM
fluctuations in the model’s ammonium pool, however, these fluctuations accounted only for 23-55% of the modeled decrease in ammonium between the two years.

A decrease in bacterial biomass to < 0.5 mg C m⁻³ (Figs 53a and 54a) by means of two-fold reduction of bacterial growth rate, on the other hand, led to more dramatic changes for both scenarios. With little bacterial ammonification ammonium concentrations stayed negligible, <0.7 µM, during both modeled years (Figs 53b and 54b). In the absence of bacteria, small ammonium flux of 2-3 mmol NH₄ m⁻² d⁻¹ produced by just zooplankton (compare to 8-13 mmol NH₄ m⁻² d⁻¹ of the total ammonium production of original model in Fig. 51) was all consumed by phytoplankton. Still, f-ratio was >0.8 for the modeled growing seasons of 2000-2001 and 2001-2002. Since ammonium flux was insufficient to satisfy phytoplankton nitrogen demands for the model cases with low bacterial growth, the timing and magnitude of phytoplankton blooms reduced somewhat, in particular for the first year scenario (Figs. 53c and 54c). Also, with greatly diminished growth rate of bacteria, up to 70 µM of unutilized DOC accumulated in the euphotic zone during summer months (Figs 53d and 54d). Light attenuation by these large DOC pools might have been another factor limiting phytoplankton growth for model cases 3 and 4.

These simulations showed that bacteria were the primary source of ammonium in the Marguerite Bay model: bacterial ammonification was essential for both build up of the model’s ammonium stocks and to satisfy model’s phytoplankton nitrogen requirements. Model’s zooplankton excretion alone could not produce substantial ammonium concentrations (>1 µM). Yet, 50% of the model’s reduction of ammonium
Fig. 53. Case 3: simulated annual cycles of (a) bacteria (mg C m\(^{-3}\)), (b) ammonium (\(\mu M\)), (c) total chlorophyll (mg chl \(a\) m\(^{-3}\)), and (d) sum of monomeric DOC\(_1\) and macromolecular DOC\(_2\) (\(\mu M\)) for the 2000-2001 scenario with maximal bacteria growth rate of 0.16 d\(^{-1}\).

Fig. 54. Case 4: simulated annual cycles of (a) bacteria (mg C m\(^{-3}\)), (b) ammonium (\(\mu M\)), (c) total chlorophyll (mg chl \(a\) m\(^{-3}\)), and (d) sum of monomeric DOC\(_1\) and macromolecular DOC\(_2\) (\(\mu M\)) for the 2001-2002 scenario with maximal bacteria growth rate of 0.16 d\(^{-1}\).
concentrations from autumn 2001 to autumn 2002 can be explained by a decrease in zooplankton biomass.

4.3.5. *Nitrification as a sink for ammonium in Marguerite Bay during 2000-2001 and 2001-2002*

There were only a few measurements of nitrification rates in the Antarctic waters. Olson (1980) and Priscu et al. (1991) found nitrification rates ranging from undetectable to 0.01 μM d⁻¹ during summer in the Ross Sea. Dore et al. (1993) estimated nitrification rates to be no more than few nM d⁻¹ in the coastal areas west of the Antarctic Peninsula during winter. A similar rate of ~4 nM d⁻¹ based on the differences between the observed ammonium concentrations in April-May 2001 and July-August 2001 was estimated for the Marguerite Bay area in section 2.5. However, preliminary model runs indicated that a nitrification rate as high as 0.02 μM d⁻¹ was needed to reduce the model’s upper water column ammonium concentrations from ~5 μM simulated for April-May 2001 to ~2 μM simulated for late July 2001 (Fig. 41). This rate was rather similar to that of 20-30 nM d⁻¹ observed by Bianchi et al. (1997) in the Atlantic sector of the Southern Ocean.

During each year, the model’s integrated water column nitrification ranged from 1.7 mmol NO₃ m⁻² d⁻¹ to 2.9 mmol NO₃ m⁻² d⁻¹ (Fig. 55). The minimal values were simulated in early spring, when ammonium concentrations were minimal (Figs. 41b, d). The maximal nitrification occurred during the months of the highest ammonium stocks, in late autumn – early winter (Fig. 55). The year to year variability in nitrification was insignificant relative to seasonal variability. Thus, in the model nitrification did not contribute to the reduction of ammonium concentrations between the two years.
Figure 55. Simulated time series of total water column nitrification (mmol NH4 m\(^{-2}\) d\(^{-1}\)) for the 2000-2001 and 2001-2002 scenarios in Marguerite Bay.

The discrepancy between the low nitrification rate of 0.004 \(\mu\)M d\(^{-1}\) estimated earlier in section 2.5 and the model’s nitrification rate of 0.02 \(\mu\)M d\(^{-1}\) was due to the following. In model simulations of 2000-2001 and 2001-2002, ammonium production by bacteria and zooplankton continued in May and June (Fig. 51) – the months after the autumnal field data were collected. Moreover, background production of ammonium by bactioves added 1.5 mmol NH4 m\(^{-2}\) d\(^{-1}\) during the winter and spring months. Thus, a higher ammonium oxidation rate was required for reduction of ammonium stocks during the winter than that based on a difference in ammonium concentrations between autumn and winter.

How important were nitrification ammonium losses compared to other ammonium removal processes within the mixed layer between autumn and winter? In 2001, ~0.32 mol m\(^{-2}\) of ammonium were oxidized to nitrate between May and August. Only approximately half of the total nitrification losses occurred in the mixed-layer. The remaining part was nitrified below the mixed layer. Losses of ammonium to phytoplankton were negligible (Fig. 42a). Integrated loss of ammonium due to lateral
exchange with low-ammonium waters between May and August was ~0.22 mol m\(^{-2}\).

After summing up all the losses, nitrification accounted for ~30% of mixed-layer ammonium losses between autumn and winter.

4.3.6. Modeling the nutrient changes in Marguerite Bay between 2000-2001 and 2001-2002

This model study supports the linkage between the seasonal sea-ice dynamics and biogeochemical cycles in the Antarctic coastal waters. The timing of sea ice retreat and advance and percentage of sea ice melted during the growing season were the major environmental factors that changed in Marguerite Bay between two years (Figs 31 and 32, Table 8). In 2000-2001, Marguerite Bay sea ice cover started to disappear in December of 2000 (Fig. 31b) allowing for rapid development of the model’s phytoplankton bloom (Fig. 45a). It quickly depleted upper water column nitrate stocks (Fig. 41a), with subsequent build up of high DOC, bacterial and ammonium pools (Figs 50a, b and 41b).

In 2001-2002, greater sea ice concentration in Marguerite Bay restricted light availability for water column phytoplankton during spring and summer (Fig. 32). Somewhat reduced sea ice cover allowed the model’s phytoplankton bloom to develop by February, at the end of the short Antarctic summer (Fig. 46a). Consequently, lower drawdown of nutrients (Fig. 41c), and a smaller dissolved organic matter stocks and bacterial biomass (Fig. 50c, d) were simulated in the second year compared to the first one. The simulated autumnal ammonium stocks, in agreement with observations, also declined from the first year to the next (Figs. 41b, d and 44).
Net community production (NCP), a representation of the whole growing season production of the plankton community, can be treated as a difference between the autotrophic production and the community respiration. Taking total DIN uptake integrated over the growing season as a proxy for autotrophic production and total ammonium production as an estimate of community respiration, the model’s N-equivalents of NCP were 0.92 mol N m$^{-2}$ and 0.64 mol N m$^{-2}$ in 2001 and 2002, respectively. They agreed favorably with Def (TIN) estimates for Marguerite Bay (Table 7).

Model’s maximal autumnal ammonium stocks integrated from the surface to the depth of zero ammonium concentrations were 0.38 mol NH$_4$ m$^{-2}$ and 0.21 mol NH$_4$ m$^{-2}$ for 2000-2001 and 2001-2002 model scenarios, respectively. They compared well to the ammonium stocks calculated from observations in Marguerite Bay during autumns of 2001 and 2002 (Table 7). A combination of two factors caused the decrease in model’s ammonium concentrations between the two years. Firstly, since ammonifying bacteria were found to be the primary source of ammonium in the Marguerite Bay model, lower primary production led to lower bacterial ammonification and, hence, lower ammonium concentrations during the second modeled year. Second, observed reduction in zooplankton stocks, primarily krill and copepods, had its effect on ammonium production. Up to 50% of the decrease in the model’s ammonium concentration between the two years was due to lower zooplankton stocks in autumn of 2002 compared to those in autumn of 2001.
4.3.7. Sensitivity analysis

The set of biological parameters employed in the model (Table 10) was largely derived from observations from the Southern Ocean. However, some were determined experimentally during model runs. To explore the sensitivity of the model to variability of the parameter values, each parameter was perturbed by ±50% of its value. The model’s maximal chlorophyll a concentration, maximal bacterial biomass, minimal nitrate concentration, maximal ammonium concentration, integrated annual primary production, and NCP were selected as diagnostics (Table 13). >10% variability for the values of the model diagnostic results was chosen as a criterion of model’s strong response to parameter perturbation.

Perturbing the maximal growth rate and saturation light intensity for diatoms had the strongest effect on the model’s results for both years (Table 13). 50% decrease in diatom growth rate led to suppression of diatom growth under model conditions. Diatom biomass was <0.01 mg chl a m\(^{-3}\) for both model scenarios. On the other hand, biomass of the model other phytoplankton groups, cryptophytes and prymnesiophytes, was somewhat higher than in the original model (Fig. 56a, b and 57a, b). However, although annual primary production of phytoplankton was ~20-30% greater in the model cases with \(\mu_D\) -50% and \(I_{SD}\) -50% than that in the original model scenarios with \(\mu_D = 0.7 \text{ d}^{-1}\) and \(I_{SD} = 45 \text{ Wm}^{-2}\), high grazing losses of cryptophytes and high lysis losses of prymnesiophytes kept total chlorophyll concentrations to be <5 mg chl a m\(^{-3}\) (Table 13). Accumulation of large concentrations of DOC of >90 \(\mu\text{M}\), build up of high bacteria stocks and ammonium concentrations as high as 8.2 \(\mu\text{M}\) for the model’s first year scenario and >4 \(\mu\text{M}\) for 2001-2002 followed mixed cryptophyte and prymnesiophyte
Table 13. Sensitivity of the selected model results (maximum chlorophyll concentration (mg chl a m$^{-3}$), maximal bacterial biomass (mg C m$^{-3}$), minimal nitrate concentration (μM), maximal ammonium concentration (μM), annual primary production (APP) of POC (g C m$^{-2}$ yr$^{-1}$), and Net community production (NCP) (mol N m$^{-2}$) to perturbation of each parameter by ±50% of its value for 2000-01 and 2001-02 model scenarios. Data in bold – strong model response, i.e. model results differ by >10% from those in the original reference model.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Max chl a</td>
<td>Max bacteria</td>
</tr>
<tr>
<td>(a) Diatoms</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maximum growth rate (d$^{-1}$), $\mu$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.35</td>
<td>4.8</td>
<td>7.2</td>
</tr>
<tr>
<td>0.70</td>
<td>20.8</td>
<td>5.6</td>
</tr>
<tr>
<td>1.05</td>
<td>28.4</td>
<td>5.6</td>
</tr>
<tr>
<td>Saturation intensity (W m$^{-2}$), $I_s$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22.5</td>
<td>28.5</td>
<td>5.6</td>
</tr>
<tr>
<td>45</td>
<td>20.8</td>
<td>5.6</td>
</tr>
<tr>
<td>67.5</td>
<td>17.0</td>
<td>5.9</td>
</tr>
<tr>
<td>Fraction of biomass respired, $\varepsilon$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.005</td>
<td>22.8</td>
<td>5.6</td>
</tr>
<tr>
<td>0.010</td>
<td>20.8</td>
<td>5.6</td>
</tr>
<tr>
<td>0.015</td>
<td>18.6</td>
<td>5.6</td>
</tr>
<tr>
<td>0.015*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fraction of biomass autolysed as DOC$_2$, $\eta$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.005</td>
<td>22.3</td>
<td>5.2</td>
</tr>
<tr>
<td>0.010</td>
<td>20.8</td>
<td>5.6</td>
</tr>
<tr>
<td>0.015</td>
<td>19.2</td>
<td>5.7</td>
</tr>
</tbody>
</table>
Table 13 (continued).

| Fraction of growth excreted as DOC<sub>1, ψ</sub> |
|-----------------|---|---|---|---|---|---|
| 0.05            | 23.1 | 4.8 | 0.4 | 4.0 | 198 [80] | 0.95 |
| 0.10            | 20.8 | 5.6 | 0.4 | 5.0 | 200 [75] | 0.92 |
| 0.15            | 18.0 | 6.0 | 0.4 | 5.9 | 203 [ ]  | 0.90 |
| 0.15*           |     |     |     |     |         |     |

| Sinking velocity (m d<sup>-1</sup>)<sub>, w</sub> |
|-----------------|---|---|---|---|---|---|
| 0.0005P<sup>2</sup> | 21.3 | 5.5 | 0.4 | 4.9 | 197 [76] | 0.92 |
| 0.001P<sup>2</sup>  | 20.8 | 5.6 | 0.4 | 5.0 | 200 [75] | 0.92 |
| 0.0015P<sup>2</sup> | 20.3 | 5.6 | 0.4 | 5.1 | 198 [75] | 0.91 |

| (b) other phytoplankton Protozoan grazing rate on cryptophytes, γ<sub>P</sub> |
|-----------------|---|---|---|---|---|---|
| 0.0625P        | 20.0 | 5.6 | 0.4 | 5.0 | 211 [67] | 0.95 |
| 0.125P         | 20.8 | 5.6 | 0.4 | 5.0 | 200 [75] | 0.92 |
| 0.1875P        | 21.0 | 5.5 | 0.4 | 5.0 | 193 [79] | 0.90 |

| Cryptophyte sinking velocity (m d<sup>-1</sup>)<sub>, w</sub> |
|-----------------|---|---|---|---|---|---|
| 0.0125          | 20.8 | 5.6 | 0.4 | 5.0 | 200 [75] | 0.92 |
| 0.025           | 20.8 | 5.6 | 0.4 | 5.0 | 200 [75] | 0.92 |
| 0.0375          | 20.8 | 5.6 | 0.4 | 5.0 | 200 [75] | 0.92 |

| Prymnesiohyte: fraction of growth excreted as DOC<sub>1, ψ</sub> |
|-----------------|---|---|---|---|---|---|
| 0.20            | 18.6 | 5.8 | 0.4 | 5.2 | 216 [62] | 0.94 |
| 0.40            | 20.8 | 5.6 | 0.4 | 5.0 | 200 [75] | 0.92 |
| 0.60            | 22.2 | 5.2 | 0.4 | 4.6 | 192 [82] | 0.92 |

| Prymnesiohyte sinking velocity (m d<sup>-1</sup>)<sub>, w</sub> |
|-----------------|---|---|---|---|---|---|
| 0.0005P<sup>2</sup> | 20.8 | 5.6 | 0.4 | 5.0 | 200 [75] | 0.92 |
| 0.001P<sup>2</sup>  | 20.8 | 5.6 | 0.4 | 5.0 | 200 [75] | 0.92 |
| 0.0015P<sup>2</sup> | 20.8 | 5.6 | 0.4 | 5.0 | 200 [75] | 0.92 |

| 19.5 | 2.4 | 4.0 | 2.4 | 166 [72] | 0.71 |
| 17.2 | 2.6 | 4.1 | 2.8 | 170 [65] | 0.64 |
| 5.2  | 3.0 | 4.7 | 4.5 | 200 [7]  | 0.62 |
| 16.8 | 2.6 | 4.0 | 3.0 | 170 [64] | 0.66 |

171
Table 13 (continued).

<table>
<thead>
<tr>
<th></th>
<th>$K_{\text{NO}_3}$</th>
<th>$K_{\text{NH}_4}$</th>
<th>$\mu_B$</th>
<th>$m$</th>
<th>$K_{\text{DOC}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(c) all phytoplankton</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Half saturation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>constant of NO$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>uptake, $K_{\text{NO}_3}$</td>
<td>0.43</td>
<td>21.0</td>
<td>5.6</td>
<td>0.3</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>0.87</td>
<td>20.8</td>
<td>5.6</td>
<td>0.4</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>1.30</td>
<td>20.5</td>
<td>5.5</td>
<td>0.6</td>
<td>4.9</td>
</tr>
<tr>
<td>Half saturation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>constant of NH$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>uptake, $K_{\text{NH}_4}$</td>
<td>0.085</td>
<td>20.7</td>
<td>5.6</td>
<td>0.4</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>0.17</td>
<td>20.8</td>
<td>5.6</td>
<td>0.4</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>20.8</td>
<td>5.6</td>
<td>0.4</td>
<td>5.1</td>
</tr>
<tr>
<td>(d) bacteria</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maximum growth rate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>($d^{-1}$), $\mu_B$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.16</td>
<td>20.6</td>
<td>0.53</td>
<td>0.4</td>
<td>0.7</td>
<td>177 [73]</td>
</tr>
<tr>
<td>0.32</td>
<td>20.8</td>
<td>5.6</td>
<td>0.4</td>
<td>5.0</td>
<td>200 [75]</td>
</tr>
<tr>
<td>0.48</td>
<td>22.8</td>
<td>9.1</td>
<td>0.5</td>
<td>4.3</td>
<td>227 [78]</td>
</tr>
<tr>
<td>Mortality rate ($d^{-1}$), $m$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.03</td>
<td>22.5</td>
<td>12.8</td>
<td>0.5</td>
<td>4.1</td>
<td>216</td>
</tr>
<tr>
<td>0.06</td>
<td>20.8</td>
<td>5.6</td>
<td>0.4</td>
<td>5.0</td>
<td>200</td>
</tr>
<tr>
<td>0.09</td>
<td>20.7</td>
<td>0.86</td>
<td>0.4</td>
<td>1.1</td>
<td>182</td>
</tr>
<tr>
<td>Half saturation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>constant of DOC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>uptake, $K_{\text{DOC}}$</td>
<td>0.415</td>
<td>20.8</td>
<td>5.5</td>
<td>0.4</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>0.83</td>
<td>20.8</td>
<td>5.6</td>
<td>0.4</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>1.245</td>
<td>20.8</td>
<td>5.5</td>
<td>0.4</td>
<td>5.0</td>
</tr>
</tbody>
</table>
Table 13 (continued).

<table>
<thead>
<tr>
<th></th>
<th>(e) zooplankton</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>% of ingested POM to DIC and to pellets (crustaceans)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>32.5 and 67.5</td>
<td>20.8 5.5 0.4 4.0 195 1.0</td>
<td>16.8 2.6 3.8 2.4 169 0.72</td>
</tr>
<tr>
<td>65 and 35</td>
<td>20.8 5.6 0.4 5.0 200 0.92</td>
<td>17.2 2.6 4.1 2.8 170 0.64</td>
</tr>
<tr>
<td>95.5 and 4.5</td>
<td>20.8 5.6 0.4 6.0 199 0.67</td>
<td>17.4 2.6 4.7 3.0 171 0.57</td>
</tr>
<tr>
<td>% of ingested POM to DIC and to pellets (protozoa)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30 and 70</td>
<td>20.4 5.5 0.4 4.8 193 0.95</td>
<td>16.4 2.6 2.9 2.7 168 0.72</td>
</tr>
<tr>
<td>60 and 40</td>
<td>20.8 5.6 0.4 5.0 200 0.92</td>
<td>17.2 2.6 4.1 2.8 170 0.64</td>
</tr>
<tr>
<td>90 and 10</td>
<td>20.9 5.6 0.4 5.2 202 0.88</td>
<td>17.5 2.6 5.7 2.8 171 0.56</td>
</tr>
<tr>
<td>Fecal pellet lysis, $\tau$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.025</td>
<td>20.8 5.5 0.4 5.0 197 0.93</td>
<td>17.2 2.6 4.1 2.7 170 0.65</td>
</tr>
<tr>
<td>0.05</td>
<td>20.8 5.6 0.4 5.0 200 0.92</td>
<td>17.2 2.6 4.1 2.8 170 0.64</td>
</tr>
<tr>
<td>0.075</td>
<td>20.8 5.6 0.4 5.0 197 0.90</td>
<td>17.2 2.6 4.1 2.7 170 0.62</td>
</tr>
</tbody>
</table>

* - model cases with reduced zooplankton grazing stress
Fig. 56. Simulated annual cycles of (a) cryptophyte biomass (mg chl a m$^{-3}$), (b) prymnesiophyte biomass (mg chl a m$^{-3}$), (c) nitrate concentration (µM), (d) ammonium concentration (µM), (e) DOC$_1$+DOC$_2$ (µM), and (f) bacteria (mg C m$^{-3}$) for the 2000-2001 scenario with maximal diatom growth rate $\mu=0.35$ d$^{-1}$.
Fig. 57. Simulated annual cycles of (a) cryptophyte biomass (mg chl \( \mu \text{m}^{-3} \)), (b) prymnesiophyte biomass (mg chl \( \mu \text{m}^{-3} \)), (c) nitrate concentration (\( \mu \text{M} \)), (d) ammonium concentration (\( \mu \text{M} \)), (e) DOC_{1} + DOC_{2} (\( \mu \text{M} \)), and (f) bacteria (mg C m^{-3}) for the 2001-2002 scenario with maximal diatom growth rate \( \mu = 0.35 \) d^{-1}. 

175
blooms (Figs 56 and 57). Although such development seems favorable in terms of my search for possible scenarios of accumulation of high ammonium stocks in Marguerite Bay, it is unlikely to occur since non-diatom blooms have not been observed in the bay. Yet, it might be a possible scenario for other Antarctic areas, such as the southwestern Ross Sea and Prydz Bay, which are well known for the large blooms of *Phaeocystis antarctica* (Schoemann et al., 2005).

Just the opposite development was observed when the model’s diatom maximal growth rate was increased by 50%. Diatoms fully dominated the phytoplankton community both in biomass and integrated annual primary production (Table 13). With diatom’s maximal growth rate being 1.05 d⁻¹, chlorophyll concentrations reached 28 mg chl a m⁻³ for 2000-2001 scenario (Fig. 58a) and 24 mg chl a m⁻³ for 2001-2002 scenario (Fig. 59a), integrated annual primary production and NCP increased by >10% (Table 13). Yet, the annual evolution of the other model outputs, i.e. nitrate, ammonium and DOC concentrations and bacteria biomass (Figs. 58 and 59) did not vary significantly from those of the reference model (Figs. 41, 50). Maximal concentrations of ammonium and bacteria and minimal concentration of nitrate changed by <10% compared to those of the original reference model scenarios (Table 13). In contrast to the cases with $\mu_D = 0.35$ d⁻¹ described earlier, this scenario is not entirely unlikely to develop in Marguerite Bay since diatom growth rates as high as 1.0 d⁻¹ have been reported for the Southern Ocean (Smith et al., 1999b).

The differences in NCP production between the two cases were remarkable (Table 13). Since most of the model’s primary production of cryptophytes and
Fig. 58. Simulated annual cycles of (a) total chlorophyll a biomass (mg chl a m$^{-3}$), (b) nitrate concentration (µM), (c) ammonium concentration (µM), (d) DOC$_1$+DOC$_2$ (µM), and (e) bacteria (mg C m$^{-3}$) for the 2001-2002 scenario with maximal diatom growth rate $\mu$=1.05 d$^{-1}$. 
Fig. 59. Simulated annual cycles of (a) total chlorophyll biomass (mg chl a m$^{-3}$), (b) nitrate concentration (µM), (c) ammonium concentration (µM), (d) DOC$_1$+DOC$_2$ (µM), and (e) bacteria (mg C m$^{-3}$) for the 2001-2002 scenario with maximal diatom growth rate $\mu = 1.05$ d$^{-1}$. 
prymnesiophytes was recycled within the upper water column by microzooplankton and bacteria as noted in section 4.3.2, a lesser amount of organic matter was exported in the model cases with no or little diatom growth than in the original scenarios. In contrast, when diatoms dominated the model’s phytoplankton community in the model cases with μ_D = 1.05 d⁻¹, the largest part of the organic matter accumulated by diatoms was exported, leading to the large NCP values.

Perturbing light parameter I_5, saturation intensity for growth, for diatoms led to similarly strong responses of model results (Table 13). With I_5 -50%, the model diatoms became more shade-adapted and followed the same development as in the case with elevated maximal growth rate. Increasing I_5 by half diminished diatom chances to dominate the phytoplankton community. Diatoms accounted only for 52% of annual primary production during the 2000-2001 model scenario and were suppressed during the 2001-2002 scenario (Table 13). This difference of model responses between two years indicated the greater effect of light limitation on diatoms under the second year conditions compared to the first year. The model’s shift to regeneration- dominated cryptophyte + prymnesiophyte scenario also resulted in the greater maximal ammonium concentration and a decline in NCP (Table 13).

One of the major points requiring testing was the uncertain parameterization of phytoplankton losses, i.e. respiration, release of monomeric DOC, and autolysis. There were only a few estimates of the magnitudes of these losses available for the Southern Ocean phytoplankton. Yet, adequate parameterization of the rates of diatom respiration, excretion and lysis was required to fuel the model’s DOC pool, which was utilized by model’s ammonifying bacteria, and, therefore, to replicate the observed 2001 and 2002
ammonium concentrations. The first year scenario of the model appeared robust. Most of
the model’s diagnostics were nearly unaffected, i.e. showed <10% variability, to the
perturbation of the diatom loss parameters (Table 13). A decline in the maximal bacterial
biomass and the maximal ammonium concentrations nevertheless occurred since the rates
of diatom losses to DOC$_1$ and DOC$_2$ pools were decreased by 50%. On the other hand,
the 50% increment of the rates of DOC production led to an increase in ammonium, a
product of the model’s bacteria regeneration of dissolved organic matter (Table 13). The
greater model’s diatom losses did however result in the somewhat lower maximal
chlorophyll concentrations.

Perturbation of the diatom losses produced a stronger effect on model’s diagnostic
results for the second year scenario compare to the first year. The 50% increase of the
rates of diatom respiration, DOC$_1$ excretion, and autolysis greatly diminished model’s
diatom growth leading to previously described cryptophyte and prymnesiophyte bloom
scenario (Table 13). Such a model response again stressed the greater growth limitation
was light, the availability of which declined from 2000-2001 to 2001-2002 due to the
greater ice cover during the second year. Secondly, considerable grazing pressure was
imposed on the model’s diatoms (Table 11). With a 2-fold reduced grazing stress during
the 2001-2002 model’s December-February, diatoms were able to win over
prymnesiophytes and cryptophytes (Table 13). Thus, elevated primary production and
biomass losses reduced the model’s diatom chances to compete with shade adapted
phytoplankton only under low light and high grazing pressure conditions. The 2001-2002
model response to a 50% decrease of diatom loss rates followed the same pattern as that
for the 2000-2001 scenario, with a somewhat increased maximal chlorophyll biomass and reduced maximal ammonium concentrations (Table 13).

Since non-diatom phytoplankton constitute a small fraction of the Marguerite Bay phytoplankton (Garibotti et al., 2003a, b), they are likely to play a negligible role in Marguerite Bay biogeochemical cycles. Yet, it was reasonable to test the model’s response to perturbation of the factors limiting growth of the model’s cryptophytes and prymnesiophytes. These factors were grazing for cryptophytes and DOC excretion for prymnesiophytes. The effect of variability of the rates of protozoan grazing (γ_p) on cryptophytes and prymnesiophyte excretion (ψ) on cryptophyte and prymnesiophyte biomass was illustrated in Fig. 48 (Section 3.3.2). Although the 50% perturbation of γ_p and ψ significantly affected the values of maximal chlorophyll biomass of these two phytoplankton groups, it produced rather a weak response of the model’s diagnostic outputs (Table 13). Interestingly, the 50% decrease of the prymnesiophyte DOC_1 excretion rate actually increased DOC availability to the bacteria that produced a somewhat higher maximal ammonium concentration than in the original reference case with ψ = 0.40 (Table 13). The greater biomass of prymnesiophytes in the model’s case with ψ = 0.20 (Fig. 48b) led to the greater production of dissolved organic matter. However, this scenario also somewhat diminished the diatom fraction of the model’s integrated annual primary production.

The Marguerite Bay model exhibited little sensitivity to variations in the sinking velocities of model’s phytoplankton (Table 13). Also, I did not observe a strong model response to perturbations of the half saturation constants of nitrate (K_{N03}) and ammonium (K_{NH4}) uptake (Table 13).
The perturbation of bacterial growth parameters had a strong impact on the model results. Some of the effects of reducing maximal bacterial growth rate, $\mu_B$, by 50% were discussed in section 3.3.4. The maximal chlorophyll biomass for $\mu_B=0.16$ d$^{-1}$ did not vary significantly from the original reference scenarios with $\mu_B=0.32$ d$^{-1}$ (Table 13). Yet, model’s integrated annual primary production declined since less ammonium was available for phytoplankton growth. NCP values, in turn, increased significantly for both model year scenarios as a result of lower remineralization of dissolved organic matter. The same model response was found for the 50% increment of bacterial mortality rate, $m_B$ (Table 13).

In contrast, increasing bacterial maximum growth rates or decreasing bacterial mortality resulted in rapid accumulation of a large bacterial biomass of $> 8$ mg C m$^{-3}$ for the 2000-2001 scenario and $>6$ mg C m$^{-3}$ for the 2001-2002 scenario (Table 13, Figs 60a and 61a). Efficient utilization of model’ DOC by bacteria did not allow accumulation of the DOC concentrations greater than 20 $\mu$M during 2000-2001 (Fig. 60b) and 10 $\mu$M during 2001-2002 (Fig. 61b) and resulted in the increased ammonium production during model’s summer. Subsurface ammonium maxima of $>3.5$ $\mu$M in 2000-2001 (Fig. 60c) and $>2$ $\mu$M in 2001-2002 (Fig. 61c) accumulated during the model’s January-February. However, since most of the model’s DOC was utilized by bacteria during the model’s summer, somewhat reduced ammonium concentrations were simulated by the model’s autumn compared to those of the original model scenarios with $\mu_B = 0.32$ d$^{-1}$ (Fig. 39b, d). Yet, greater summer-time ammonium regeneration may lead to an $f$-ratio as low as the 0.2-0.3 observed near the northern tip of Antarctic Peninsula (Koike et al., 1986; Owens
Fig. 60. Simulated annual cycles of (a) bacteria (mg C m\(^{-3}\)), (b) DOC\(_1\)+DOC\(_2\) (µM), (c) ammonium concentration (µM), (d) nitrate concentration (µM), and (e) total chlorophyll biomass (mg chl a m\(^{-3}\)) for the 2000-2001 scenario with maximal bacteria growth rate µ=0.48 d\(^{-1}\).
(a) Bacteria (mg C m$^{-3}$) 

(b) DOC$_1$+DOC$_2$ (µM) 

(c) Ammonium (µM) 

(d) Nitrate (µM) 

(e) Total chlorophyll (mg chl a m$^{-3}$) 

Fig. 61. Simulated annual cycles of (a) bacteria (mg C m$^{-3}$), (b) DOC$_1$+DOC$_2$ (µM), (c) ammonium concentration (µM), (d) nitrate concentration (µM), and (e) total chlorophyll biomass (mg chl a m$^{-3}$) for the 2001-2002 scenario with maximal bacteria growth rate $\mu=0.48$ d$^{-1}$. 

184
et al., 1991). Indeed, increasing bacterial biomass is a recipe for the smaller $f$-ratios. In the model’s cases with $\mu_B = 0.48$ d$^{-1}$ and $m_B = 0.03$ d$^{-1}$, average $f$-ratios were <0.6 during the model’s summer. As a result of the greater ammonium uptake, less nitrate was consumed by phytoplankton. For example, in the 2001-2002 scenario, nitrate concentrations were never depleted below 9 $\mu$M (Table 13, Fig. 60d). Since high bacterial biomass has been indeed observed in the Antarctic waters (Karl et al., 1991; Clarke and Leakey, 1996), increasing $\mu_B$ or decreasing $m_B$ are plausible modeling scenarios that lead to high phytoplankton production (Table 13) and simulate relatively high ammonium concentrations throughout model’s summer and autumn. Although these scenarios resulted in somewhat lower NCP values (Table 13), they were still within the range of the values observed in Marguerite Bay in autumns of 2001 and 2002 (Table 7).

Perturbation of the other bacterial model parameter, the half saturation constant of DOC uptake $K_{SDOC}$, had no significant effect on the model’s outputs (Table 13).

Among the zooplankton model parameters, fractions of ingested particulate organic matter excreted as DIC and $NH_4$ versus that converted to fecal pellets for both crustaceans and protozoa and fecal pellet lysis rate were tested with sensitivity analysis (Table 13). As expected, the primary effect of variability in the proportion of POM excreted was on the maximal ammonium concentration and NCP. Since zooplankton pellets had high sinking rates in the model, they made insignificant contribution to DOC pool, and therefore to ammonium production. Thus, increasing the fraction of POM respired resulted in higher modeled ammonium concentrations and lower modeled NCP values, since NCP was a difference between phytoplankton production and community
respiration. In contrast, increasing pellet production led to a decline of ammonium concentrations and an increase in the export production.

To sum up, the model showed little sensitivity to perturbation of most of the parameters. The model’s results were most sensitive to variations of the maximal growth parameters of diatoms and bacteria and light parameter $I_5$. Yet, observations from Marguerite Bay and similar Antarctic coastal areas strongly suggested that the model’s scenarios with the lowered growth rates or elevated $I_5$ were not realistic. On the other hand, the model outputs simulated with high-end values for the growth parameters did not contradict the observations. The model results were somewhat sensitive to the phytoplankton loss parameters, for which there were few quantitative observations. However, when the effects of light limitation and grazing pressure were considered, the model was proved robust to the perturbations of the loss parameters.

4.4. Model conclusions

A biogeochemical model was applied to Marguerite Bay in order to investigate the cycles of nitrogen and carbon through the Marguerite Bay dissolved inorganic pools and plankton communities during the 2000-2001 and 2001-2002 austral years. The model nutrient fields compared favorably to the observations made during the LTER and SO GLOBEC surveys in 2001-2002. The seasonal cycles of chlorophyll, bacteria, and dissolved organic matter captured by the model were in agreement with previous observations in Marguerite Bay and/or other similar Antarctic coastal areas.

The following conclusions can be drawn from the Marguerite Bay model:

Sea ice cover can be a factor determining the magnitude of phytoplankton production and phytoplankton community structure in Marguerite Bay. Somewhat greater
ice cover applied for the model’s 2001-2002 scenario led to ~15% reduction of the integrated annual primary production (APP), the diatom’s portion of APP, and the chlorophyll stocks between the two modeled years. Moreover, a decrease in primary production between the two years resulted in the lower bacterial production in 2001-2002 compared to that in 2000-2001, since phytoplanktonic release of dissolved organic matter and phytoplanktonic debris were the major sources of bacterial growth in the model.

Bacterial ammonification was found to be the primary source of ammonium in the Marguerite Bay model. Hence, reduced bacterial ammonification led to somewhat lower production of ammonium in 2001-2002 compared to that in 2000-2001. Yet, variability in zooplankton stocks accounted for 15-25% of the fluctuations in ammonium concentration and, hence, translated to up to 50% of the difference in ammonium concentrations between the two modeled years.

Greater sea ice cover did not result in the greater model’s nitrification in 2001-2002 compared to 2000-2001. Yet, nitrification accounted for ~30% of the model’s wintertime decline in ammonium concentrations during both modeled years.

Since bacterial ammonification was the primary source of ammonium and dissolved organic matter of phytoplanktonic origin was the primary substrate for ammonifying bacteria in the Marguerite Bay model, adequate parameterization of the phytoplankton losses to the DOM pool was an important subject to consider. Sensitivity analysis showed that if the rates of phytoplankton losses were chosen to be too high, they led to suppression of diatom growth and development of unobserved blooms of cryptophytes and prymnesiophytes under the conditions of light limitation and moderate
grazing pressure. On the other hand, if these rates were chosen to be too low, model gave reasonable results, although ammonium concentrations were underestimated.

Sensitivity analysis provided some interesting insights into Net Community Production (NCP). It showed that NCP, for instance, largely depended on the phytoplankton community structure. Model’s NCP values were not necessarily correlated with the magnitude of primary production. In the model cases with diatoms dominating phytoplankton community most of the organic matter accumulated was exported, leading to high NCP values. In the model cases with high primary production rates of prymnesiophytes and cryptophytes, regeneration dominated over the export and, consequently, NCP values were lower. Yet, within the same model’s phytoplankton community structure, the greater primary production led to a larger export production. Thus, care should be taken while comparing NCP values for different biogeochemical regimes.
References


Ross, R.M., Quetin, L.B., 2001. Zooplankton Data from LTER. LTER data system, online, dataset, http://pal.lternet.edu/cgi-bin/ucmbo-cgi/studycatalog03.cgi.

Ross, R.M., Quetin, L.B., 2002. Zooplankton Data from LTER. LTER data system, online, dataset, http://pal.lternet.edu/cgi-bin/ucmbo-cgi/studycatalog03.cgi.


Vernet, M. 2001. Chlorophyll and Nutrient Data from LTER. LTER data system, online, dataset, http://pal.lternet.edu/cgi-bin/ucmbo-cgi/studycatalog03.cgi.


About the Author

Yulia Serebrennikova received a Bachelor’s of Science degree in Chemistry and Ecology from the Novosibirsk State University, Russia, in 1998. She received a Master of Science degree in Chemistry from Novosibirsk State University in 2000. While in the MS program she was a recipient of the academician G.K. Boreskov Scholarship during the first year of research and the academician K.I. Zamaev Scholarship during her second year from Boreskov Institute of Catalysis, Novosibirsk, Russia.

Yulia Serebrennikova entered the Ph.D. program at the College of Marine Science, University of South Florida, in 2000. She participated in three open ocean cruises to the Southern Ocean abroad the R/V. Nathaniel B. Palmer as well as four local cruises to Eastern Gulf of Mexico aboard the R/V. Pelican and R/V. Walton Smith.