

# JCU ePrints

This file is part of the following reference:

**da Silva, Eduardo (2005) *Cadmium accumulation in the barnacle biomonitor *Balanus amphitrite*: combining field and laboratory observations with modelling*. PhD thesis, James Cook University.**

Access to this file is available from:

<http://eprints.jcu.edu.au/2125>



Cadmium accumulation in the barnacle biomonitor  
*Balanus amphitrite*: Combining field and laboratory  
observations with modelling

Thesis submitted by

*Eduardo Teixeira da Silva*

in September 2005

for the degree of

Doctor of Philosophy

in the

Department of Chemistry,

School of Pharmacy and Molecular Sciences,

James Cook University

## Statement of Access

I, Eduardo Teixeira da Silva, the author of this thesis, understand that James Cook University will make it available for use within the University Library and allow access to user in approved libraries. All users consulting this thesis must sign the following statement.

In consulting this thesis, I agree not to copy or closely paraphrase it in whole or in part without the consent of the author; and to make proper written acknowledgment for any assistance that I have obtained from it.

Beyond this, I do not wish to place any restrictions on access to the thesis.

---

Eduardo Teixeira da Silva

---

date

## Statement of Sources

I declare that this thesis is my own work and has been submitted in any form for another degree or diploma at any university or other institution of tertiary education. Information derived from published or unpublished work of others has been acknowledged in the text and a list of references provided.

---

Eduardo Teixeira da Silva

---

date

## Acknowledgments

I wish to acknowledge David Klumpp (Australian Institute of Marine Science) and Peter Ridd (Department of Physics – James Cook University) for their supervision and support on this study, and Michael Ridd (Department of Chemistry – James Cook University) whose support, enthusiasm, friendship and encouragement throughout this study were far beyond of a supervisor – student relationship.

I thank all the people who contributed in some aspect to this work. My special thanks to Kirsten Michalek-Wagner and staff, for their support on the non-radiochemical experiments carried out at Reef HQ – GBRMPA, and to Anna-Marie Babey, for her support of the radiochemical experiments carried out at the School of Biomedical and Veterinary Sciences – James Cook University. The support received at the Australian Institute of Marine Science provided by David McKinnon and Paul Dixon, for their valuable comments on microzooplankton field and laboratory methodology, and by Cassie Payn and Steve Boyle, for their help with the use of the Zeeman GF-AAS and the ICP-AES, is gratefully acknowledged.

I acknowledge the support provided by the James Cook University staff regarding the field operations (Phil Osmond and Gordon Bailey), technical assistance (Jeff Cavanagh), and statistical advice (Yvette Everingham and David Donald). I also thank the Townsville Port Authority for allowing the mooring operation close to the Channel Mark and for making available the tide data, and the Climate and Consultative Services Section of the Bureau of Meteorology and Russell Jaycock (Physics – James Cook University) for provision of the meteorological data recorded at the Townsville Airport. I also acknowledge Gillian Peck

(Australian Nuclear Science and Technology Organization) for the training and experience provided on the use of radioisotopes.

I acknowledge the receipt of a Scholarship to support this study from the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES, Brazil).

My very special thank to Alessandra, Giovanni and Bruno for their friendship, tenderness and love.

## Abstract

The present study addressed the need to understand how short-term variations in metal concentrations in the environment determine its concentrations in a biomonitor, and how this information affects the use of the biomonitor in environmental monitoring programs. As a case study, the barnacle biomonitor *Balanus amphitrite* present in Ross Creek (Townsville, Queensland, AU) and the heavy metal Cd were used. The research methodology for this study comprised three integrated approaches: field measurements; the performance of laboratory experiments, and the development of an ecotoxicological simulation model, in order to understand the processes controlling Cd accumulation in *Balanus amphitrite* in the field. Two sampling programs were carried out along Ross Creek, in the dry season of 2002 and the wet season of 2004, in which barnacles, their food sources (two class sizes of suspended particulate material, SPM, and microzooplankton) and water (dissolved phase) were sampled weekly for Cd concentrations and mass abundances. Sampling periods were selected to test whether the concentration of Cd in the biomonitor responded to any variation in the dissolved and particulate phase Cd concentrations in Ross Creek, as caused by rainfall variation.

In both sampling periods, the Cd concentration in the dissolved phase increased upstream, ranging from 1.6 to 283 ngL<sup>-1</sup>. The Cd concentration in the barnacle's food sources exhibited the same pattern – ranging from <0.01 to 2.10 mg kg<sup>-1</sup> for the small size class of SPM (0.45–50 µm), from 0.07 to 1.62 mg kg<sup>-1</sup> for large SPM (50–200 µm), and from 0.03 to 0.80 mg kg<sup>-1</sup> for microzooplankton (50–200 µm). The Cd concentration in two populations of *Balanus amphitrite* increased upstream between two sites 2.20 km apart and ranged from 2.15 to 6.40 mg kg<sup>-1</sup> and from 5.22 to 12.8 mg kg<sup>-1</sup>. Even though no significant temporal variation was

detected for the Cd sources to the barnacles, the biomonitor Cd concentrations varied over the three sampling months, within each sampling period, exhibiting specific patterns for this variation. These observations suggest that changes in the Cd concentrations in the food sources and the relative mass abundance of these sources may result in a specific Cd concentration in *Balanus amphitrite*.

Similar Cd concentrations, within sites, were observed for the particles between the dry and wet seasons. Only the most contaminated site exhibited significant differences in the dissolved Cd concentration between seasons. Because more than 95% of the total Cd in the Ross Creek water (<200  $\mu\text{m}$ ) was in the dissolved phase (<0.45  $\mu\text{m}$ ), the differences in the dissolved Cd concentration resulted in the barnacles from the most Cd-contaminated site being exposed to a total Cd concentration in the wet season (45.8  $\text{ng L}^{-1}$ ) that was a half of that in the dry season (91.6  $\text{ng L}^{-1}$ ). Such Cd differences were not indicated by the biomonitor whose Cd concentration did not vary significantly between dry (8.4  $\text{mg kg}^{-1}$ ) and wet (7.4  $\text{mg kg}^{-1}$ ) seasons. A budget analysis based on Thomann's bioenergetic kinetic model, indicated that Cd flux from food contributes >80% of the Cd concentration in *Balanus amphitrite*. Thus, because no significant variation was identified for the Cd concentration in the food, no variation in the Cd concentration in the biomonitor was observed at the most contaminated site between seasons. A sensitivity analysis on the model showed that physiological characteristics of the biomonitor are the key parameters controlling Cd accumulation in *Balanus amphitrite*, rather than the metal concentration in the dissolved or particulate phases. This, coupled with the fact that the Cd flux from food is the major source of Cd to *Balanus amphitrite* suggests no tight coupling between Cd in the biomonitor and its availability in the environment.



A simulation model was developed based on Thomann's bioenergetic kinetic model. The daily-simulated Cd concentration in *Balanus amphitrite* produced by the model reproduced the general trend observed in the field. However, even though high and low patterns of Cd concentration in this organism could be reproduced by the model, it could not reproduce the short-term temporal variations accurately. A model investigation suggested that variations in the mean weight of the sampled barnacles might mask the real pattern of temporal variation of the barnacles Cd concentration; even though no size effect has been identified in the field data.

Two simulation exercises indicated that *Balanus amphitrite* may present some weakness in indicating temporal variations in Cd concentrations in the environment. The model results suggested that this organism could not indicate a 6-month Cd-pulse in the environment that increased the Cd concentration in its main source (small SPM, 0.45–50  $\mu\text{m}$ ) by a factor of 2.8 using a realistic sampling effort. In addition, this organism took more than a year to reach equilibrium for its Cd concentration in a simulated relocation experiment. These problems may be critical for the use of *Balanus amphitrite* as a biomonitor, and suggest that this organism can only provides a poor measure of current bioavailability of the metal in the environment. However, if a long-term mean Cd availability in the particulate fraction (sized <200  $\mu\text{m}$ ) is required, *Balanus amphitrite* can provide such an information.

# Table of Contents

Statement of Access .....	ii
Statement of Sources .....	iii
Acknowledgments .....	iv
Abstract .....	vi
Table of Contents .....	ix
List of Tables.....	xiv
List of Figures .....	xv
List of Appendices.....	xxi
<b>Chapter 1. General introduction.....</b>	<b>1</b>
1.1. Introduction .....	1
1.2. Aims of the Study .....	4
1.3. Justification.....	5
1.3.1. The organism.....	5
1.3.2. The environment .....	6
1.3.3. The importance of this study.....	7
1.4. Thesis Outline.....	8
<b>Chapter 2. Cadmium accumulation in aquatic organisms .....</b>	<b>11</b>
2.1. Environmental Chemistry of Cd.....	11
2.1.1. Cadmium in the marine environment.....	12

2.1.2. Dealing with Cd speciation .....	14
2.1.3. Cadmium accumulation in aquatic organisms .....	16
2.1.4. Understanding metal transference using radioisotopes.....	17
2.2. Modelling Metal Accumulation in Aquatic Organisms .....	22
2.2.1. Simulation modelling: Theoretical background.....	22
2.2.2. Thomann's bioenergetic kinetic model.....	26
2.2.3. "Matching model and the real world" .....	27
<b>Chapter 3. Site description and general methodology of sampling and analyses.....</b>	<b>29</b>
3.1. Study Site.....	29
3.2. Sampling Program .....	31
3.2.1. Sample collection .....	32
3.2.2. Sample treatment.....	33
3.2.3. Cadmium determination.....	35
3.2.4. Data analyses and quality control.....	36
3.3. Seasonal Environmental Differences Between the Two Sampling Periods .....	39
<b>Chapter 4. Relative contribution of food and water to the Cd concentration in</b>	
<i>Balanus amphitrite</i> .....	41
4.1. Introduction .....	41
4.2. Results and Discussion .....	42
4.2.1. Temporal and spatial variation in abundance of the particles sized <200	
μm.....	42

4.2.2. Temporal and spatial variation of Cd concentrations in water and particles sized <200 $\mu\text{m}$ .....	45
4.2.3. Partitioning of Cd in the Ross Creek water and its export into the GBR Lagoon.....	48
4.2.4. Temporal and spatial variation of Cd in <i>Balanus amphitrite</i> .....	51
4.2.5. Biological concentration and magnification factors applied to the spatial variations of Cd concentrations in <i>Balanus amphitrite</i> .....	52
4.3. Final Remarks.....	54
<b>Chapter 5. Does <i>Balanus amphitrite</i> indicate seasonal variation in Cd concentrations in the environment? .....</b>	<b>56</b>
5.1. Introduction .....	56
5.2. Material and Methods.....	57
5.2.1. Determination of the clearance rate for <i>Balanus amphitrite</i> in the laboratory.....	57
5.2.2. Determination of the growth for <i>Balanus amphitrite</i> in the field .....	59
5.2.3. Budget analysis .....	60
5.2.4. Sensitivity analysis.....	62
5.3. Results .....	63
5.3.1. Dissolved Cd concentration .....	65
5.3.2. Particulate Cd concentration and mass abundance .....	65
5.3.3. Cadmium concentration in <i>Balanus amphitrite</i> .....	66
5.3.4. Clearance rate for <i>Balanus amphitrite</i> in the laboratory .....	68

5.3.5. Growth rate for <i>Balanus amphitrite</i> in the field .....	69
5.3.6. Budget analysis .....	70
5.3.7. Sensitivity analysis.....	72
5.4. Discussion.....	73
5.4.1. Spatial and seasonal variation of the Cd concentration in <i>Balanus amphitrite</i> .....	73
5.4.2. Budget analysis of the seasonal Cd variation in <i>Balanus amphitrite</i> .....	74
5.4.3. Sensitivity analysis of the controls on Cd concentrations in <i>Balanus amphitrite</i> .....	75
5.4.4. Effect of the growth rate on the Cd concentration in <i>Balanus amphitrite</i> .....	78
5.5. Final Remarks.....	80

**Chapter 6. Exploring the potential of *Balanus amphitrite* as a biomonitor for**

temporal and spatial variations in Cd contamination in a simulation model .....	83
6.1. Introduction .....	83
6.2. Methodology.....	84
6.2.1. Simulation model .....	84
6.2.2. Parameters for the simulation model.....	86
6.2.3. Radiochemical experiments using <sup>109</sup> Cd.....	87
6.2.3.1. Cadmium uptake rate constant from the dissolved phase .....	88
6.2.3.2. Cadmium AE from SSPM with different chlorophyll concentrations .....	90
6.2.3.3. Cadmium efflux rate constant.....	93

6.3. Results and Discussion .....	93
6.3.1. Field data used as the model's forcing functions.....	93
6.3.2. Radiochemical experiments with <sup>109</sup> Cd.....	97
6.3.2.1. Cadmium uptake rate constant from the dissolved phase .....	97
6.3.2.2. Cadmium AE from SSPM with different chlorophyll concentrations .....	101
6.3.2.3. Cadmium efflux rate constant.....	105
6.3.3. Summary of the model's parameters and baseline simulations.....	106
6.3.4. Model investigation.....	111
6.3.5. Exploring the potential for <i>Balanus amphitrite</i> as a biomonitor for Cd environmental contamination in a simulation model .....	116
6.3.5.1. Modelling effects of localized dredging operation on Cd accumulation in <i>Balanus amphitrite</i> .....	117
6.3.5.2. Modelling effects of a relocation experiment on the Cd concentration in <i>Balanus amphitrite</i> .....	121
6.4. Final Remarks.....	124
<b>Chapter 7. Summary, conclusions and recommendations for further research .....</b>	<b>126</b>
7.1. General Thesis Overview and its Major Conclusions .....	126
7.2. Environmental Management Applications .....	130
7.3. Suggestions for Further Research.....	131
<b>Literature Cited.....</b>	<b>134</b>

## List of Tables

Table 3.1: Analyses of National Research Council (Canada) certified materials for quality control purpose (mean $\pm$ 1 SD).....	38
Table 4.1: P-values (p), number of samples (n) and number of groups (ng, i.e., either number of sites or dates) for the Kruskal-Wallis test applied to the concentrations in mass and Cd of SSPM (0.45–50 $\mu\text{m}$ ), LSPM (50–200 $\mu\text{m}$ ), microzooplankton (50–200 $\mu\text{m}$ ) and Cd in the dissolved phase (<0.45 $\mu\text{m}$ ) sampled in Ross Creek from 6 August to 30 October 2002.....	45
Table 4.2: Mean Cd concentration in the dissolved phase (<0.45 $\mu\text{m}$ ), SSPM (0.45–50 $\mu\text{m}$ ), LSPM (50–200 $\mu\text{m}$ ), microzooplankton (50–200 $\mu\text{m}$ ) and <i>Balanus amphitrite</i> . The biological concentration factor between <i>Balanus amphitrite</i> and water (BCF) and the biological magnification factor between <i>Balanus amphitrite</i> and all its Cd sources (BMF) are also presented (see text for full description).....	54
Table 5.1: Cadmium concentrations, mass abundances, total Cd concentration in the Ross Creek water (sized <200 $\mu\text{m}$ ), Cd concentration in <i>Balanus amphitrite</i> and individual dry weights, sampled at sites B and C, in the wet and dry seasons (mean $\pm$ 1 SD). The Mann-Whitney test (p-value), comparing dry and wet seasons' data for each site, and the number of samples (n) are also presented. ....	64
Table 6.1: The Cd AE from different food types for <i>Balanus amphitrite</i> . ....	103

Table 6.2: Simulation model's parameters, their description/equation, units and the source of information. ....	108
Table 6.3: Model validation. Paired t-test (p-value) and the model efficiency coefficient, <i>EF</i> (Mayer & Butler 1993) comparing model results and field data of Cd concentrations in <i>Balanus amphitrite</i> . The number of pair compared (n) is also represented. ....	111

## List of Figures

Figure 2.1: Geochemical speciation of Cd (from Bourg 1995).....	13
Figure 2.2: Typical bi-phasic pattern for the variation in the percentage of <sup>109</sup> Cd activity in <i>Balanus amphitrite</i> following the 'hot' phase in the pulse-chase feeding experiment carried out in this study (see complete series of data in section 6.3.2.2). ....	20
Figure 2.3: Conceptual model of the lake system. Diagram follows the symbolic language (a) as proposed by Odum (1983), and (b) as used in the Stella software. It represents two state variables (i.e. grass and fish), two processes (production and grazing) and three forcing functions (light, nutrient and temperature). The box in upper diagram represents the limit of the system.....	24
Figure 3.1: Sampling area in Ross Creek (Townsville, Queensland), its urbanized vicinity and the location of the sampling sites (A, B, C and D). The locations of	



another two non-regular sampling sites (Lakes and Pool) and the revegetated municipal dump (black triangle) are also represented.....	30
Figure 3.2: Horizontal superficial salinity profile in Ross Creek, comparing for three tide situations: (a) a syzygy, (b) a quadrature and (c) an intermediary situation. ....	37
Figure 3.3: Temporal variation of the rainfall and evaporation (upper graphic) and the water level (lower graphic) for the dry season of 2002 (a) and the wet season of 2004 (b). Rainfall scales differ on graphics. ....	39
Figure 3.4: Mean water salinity (a) and temperature (b) measured at the low tide (LT) and at the high tide (HT) at sites A, B, C and D along Ross Creek in the dry season of 2002 and the wet season of 2004. Bars stand for $\pm 1$ SD.....	40
Figure 4.1: Mass concentration ( $\text{mg L}^{-1}$ ) of (a) SSPM ( $0.45\text{--}50\ \mu\text{m}$ ), (b) LSPM ( $50\text{--}200\ \mu\text{m}$ ) and (c) microzooplankton ( $50\text{--}200\ \mu\text{m}$ ), sampled from 6 August to 30 October 2002 in Ross Creek at site A during the high tide, A(HT), site B at high tide, B(HT) and at low tide, B(LT), and at site C at high tide, C(HT) and at low tide, C(LT).....	43
Figure 4.2: Cd concentration in (a) the dissolved phase ( $<0.45\ \mu\text{m}$ , $\text{ng L}^{-1}$ ), (b) SSPM ( $0.45\text{--}50\ \mu\text{m}$ , $\text{mg L}^{-1}$ ), (c) LSPM ( $50\text{--}200\ \mu\text{m}$ , $\text{mg L}^{-1}$ ) and (d) microzooplankton ( $50\text{--}200\ \mu\text{m}$ , $\text{mg L}^{-1}$ ), measured from 6 August to 30 October 2002 in Ross Creek at site A during the high tide, A(HT), site B at high tide, B(HT) and at low tide, B(LT), and at site C at high tide, C(HT) and at low tide, C(LT).....	47
Figure 4.3: Mean temporal variation of $K_d$ , Cd concentration in the dissolved phase and Cd concentration in the particles over the sampling sites: at site A during	

the high tide, A(HT), site B at high tide, B(HT) and at low tide, B(LT), and at site C at high tide, C(HT) and at low tide, C(LT). .....	50
Figure 4.4: Cd concentration in <i>Balanus amphitrite</i> ( $\text{mg kg}^{-1}$ ) sampled in Ross Creek at sites B and C, from 6 August to 30 October 2002. Data are means for 6–8 size class with 3–6 individuals in each, and error bars represent 1 SD.....	52
Figure 5.1: Relationship between <i>Balanus amphitrite</i> 's orifice size ( $\text{mm}^2$ ) and its individual dry weight (mg) determined from the barnacles sampled at sites B and C on April 20, 2004.....	60
Figure 5.2: Temporal variation of the mean Cd concentration in <i>Balanus amphitrite</i> ( $\text{mg kg}^{-1}$ ) sampled at sites B and C during the wet season of 2004 (a) and the dry season of 2002 (b) in Ross Creek. Error bars stand for 1 SD. ....	67
Figure 5.3: Clearance rate ( $\text{L h}^{-1} \text{mg}^{-1}$ ) as a function of the <i>Balanus amphitrite</i> individual dry weight (mg) determined in the laboratory for organisms feeding on two types of food (natural suspended particular matter from Ross Creek and the algae <i>Chaetoceros muelleri</i> ).....	68
Figure 5.4: Growth rate (dry weight-based, in $\text{d}^{-1}$ ) as a function of the <i>Balanus amphitrite</i> individual dry weight (mg) determined from photos taken in the field at both sites in the dry and wet seasons.....	70
Figure 5.5: Budget models for site B and C in the wet season of 2004 and dry season of 2002. The Cd fluxes from the dissolved phase (DISS), SSPM, microzooplankton (MZOOB) and LSPM to <i>Balanus amphitrite</i> and the decrease in Cd concentration (efflux and dilution) are represented. Cadmium fluxes (in	

brackets) are in $\mu\text{g kg}^{-1} \text{d}^{-1}$ , and Cd concentrations in barnacles (within hexagons) are in $\text{mg kg}^{-1}$ .....	71
Figure 5.6: The result of the sensitivity analysis performed on all the parameters included in Equation 5.2. Each bar represents the % variation in the <i>Balanus amphitrite</i> Cd concentration when variations of $\pm 25\%$ and $\pm 50\%$ are applied. Numbers in brackets represent the range of variation between the two extreme bars for each parameter. ....	72
Figure 5.7: Simulation of the relative Cd concentration in <i>Balanus amphitrite</i> as a function of its individual dry weight (mg) for different growth rates (values close to the curves, in $\text{mg mg}^{-1} \text{d}^{-1}$ ). ....	80
Figure 6.1: Calibration curve produced by measuring the $^{109}\text{Cd}$ activity in a blank (500 $\mu\text{L}$ of distilled water) and three standards with 0.0026, 0.0064 and 0.0128 ng of $^{109}\text{Cd}$ (i.e., activity of 44.7, 110 and 220 Bq, respectively) in 500 $\mu\text{L}$ of distilled water. The corresponding %RSD for blank and standards were 77.1, 2.47, 1.50 and 1.07. ....	89
Figure 6.2: Temporal variation of the Cd concentration in the dissolved phase (a and b, $<0.45 \mu\text{m}$ ), in $\text{ng L}^{-1}$ , and in SSPM (c and d, $0.45\text{--}50 \mu\text{m}$ ), LSPM (e and f, $50\text{--}200 \mu\text{m}$ ) and microzooplankton (g and h, $50\text{--}200 \mu\text{m}$ ), all in $\text{mg kg}^{-1}$ , sampled at sites B and C during the dry season of 2002 (graphics on left) and the wet season of 2004 (graphics on right) in Ross Creek. ....	94
Figure 6.3: Temporal variation of the mass abundance of chl <i>a</i> (a and b, in $\mu\text{g L}^{-1}$ ), and SSPM (c and d, $0.45\text{--}50 \mu\text{m}$ ), LSPM (e and f, $50\text{--}200 \mu\text{m}$ ) and microzooplankton (g and h, $50\text{--}200 \mu\text{m}$ ), all in $\text{mg L}^{-1}$ , sampled at sites B and C	

during the dry season of 2002 (graphics on left) and the wet season of 2004 (graphics on right) in Ross Creek.....	96
Figure 6.4: Cadmium uptake rates as a function of different dissolved Cd concentrations. Numbers in brackets stand for the standard error of the parameter in the adjusted model.....	98
Figure 6.5: Cadmium uptake rates as a function of three different salinities at a dissolved Cd concentration of $369 \pm 11 \text{ ng L}^{-1}$ (mean $\pm$ range). Numbers in brackets stand for the standard error of the parameter in the adjusted model.....	99
Figure 6.6: Dependence of the individual barnacles' dry weight on the ratio between the Cd uptake rate from the dissolved phase and the corresponding dissolved Cd concentration. ....	100
Figure 6.7: Retention of $^{109}\text{Cd}$ in 14 barnacles after seven of them been fed with SSPM poor in chl <i>a</i> (a) and the other seven been fed with SSPM rich in chl <i>a</i> (b). Numbers in brackets stand for the standard error of the parameter in the adjusted model. Different symbols stand for each of the seven barnacles fed with each batch of SSPM. ....	101
Figure 6.8: The Cd AE from SSPM for <i>Balanus amphitrite</i> as a function of the ratio between chl <i>a</i> abundance ( $\mu\text{g L}^{-1}$ ) and SSPM mass abundance ( $\text{mg L}^{-1}$ ) obtained from two independent measurements: 'estimated' from the steady-state model and field data, and 'measured' in the laboratory with $^{109}\text{Cd}$ and pulse chase feeding technique. See text for explanation. ....	104
Figure 6.9: Retention of $^{109}\text{Cd}$ in the four most $^{109}\text{Cd}$ active barnacles after they have been used in the experiment for the AE determination. Numbers in brackets	

stand for the standard error of the parameter in the adjusted model. Different symbols stand for each of the four barnacles. Marked white circles were not considered in the analysis because the barnacle was dead..... 106

Figure 6.10: Model's baseline simulation. Comparison between Cd concentrations in *Balanus amphitrite* simulated (line) and observed in the field (white square) at site B in the dry season of 2002 (a) and wet season 2004 (b), and at site C in the dry season of 2002 (c) and wet season 2004 (d). Error bars stand for  $\pm 1$  SD..... 109

Figure 6.11: Model's results of the simulation exercise in which barnacles' weight was considered as a state variable in the model. Comparison between Cd concentrations in *Balanus amphitrite* simulated (line) and observed in the field (white square) at site B in the dry season of 2002 (a) and wet season 2004 (b), and at site C in the dry season of 2002 (c) and wet season 2004 (d). Error bars stand for  $\pm 1$  SD..... 113

Figure 6.12: Results of the dredging operation's simulation exercise. The 'standard' scenario, in which SSPM presents its normal Cd concentration observed in the field, and the 'dredging' scenario, in which the SSPM Cd concentration was increased by a factor of 2.8 from Julian Day 90 to 270, are represented. .... 119

Figure 6.13: Simulation of the power test to detect difference between two sets of data (in this case: Cd concentrations in barnacles) as a function of the difference between them, assuming that data has a SD of  $1.63 \text{ mg kg}^{-1}$  and  $\alpha = 0.05$  for a total number of samples for both groups of 14. .... 120

Figure 6.14: Results of the relocation simulation exercise. 'Site B' and 'Site C' curves stand for the standard simulation of the Cd concentrations in *Balanus amphitrite*

living at sites B and C, respectively. The curve 'relocated' represents the Cd concentrations in a barnacle that was moved from site B to site C and *vice versa* on Julian Day 90..... 122

## List of Appendices

**Appendix I:** Energetic language as proposed by Odum (1983) and its comparison with the language used on the Stella software (Wallis et al. 2002). This is not a complete list of all the symbols; only those used on the models are presented. .... 151

**Appendix II:** All data sampled in the field in the two sampling programs, from 6 August 2002 to 30 October 2002 and from 21 January 2004 to 14 April 2004, in Ross Creek (Townsville, Queensland, AU). .... 152

**Appendix III:** Stella diagram of the simulation model. .... 155

**Appendix IV:** Computational code of the simulation model developed in the Stella software. .... 156

**Appendix V:** Stella diagram for the model used in the simulation exercise in which the mean barnacles' weight was considered as a state variable..... 159

**Appendix VI:** My response to Examiners' comments..... 160

**Appendix VII:** Published work raised from this study. .... 167