

## Southern Ocean iron fertilization by baleen whales and Antarctic krill

Stephen Nicol<sup>1,2</sup>, Andrew Bowie<sup>2</sup>, Simon Jarman<sup>1,3</sup>, Delphine Lannuzel<sup>2,4</sup>, Klaus M Meiners<sup>2</sup> & Pier van der Merwe<sup>2,5</sup>

<sup>1</sup>Department of the Environment, Water, Heritage and the Arts, Australian Antarctic Division, 203 Channel Highway, Kingston, Tas. 7050, Australia; <sup>2</sup>Antarctic Climate and Ecosystems Cooperative Research Centre, University of Tasmania, Private Bag 80, Hobart, Tas. 7001, Australia; <sup>3</sup>Department of the Environment, Water, Heritage and the Arts, Australian Antarctic Division, Australian Marine Mammal Centre, 203 Channel Highway, Kingston, Tas. 7050, Australia; <sup>4</sup>Centre for Marine Science, University of Tasmania, Private Bag 78, Hobart, Tas. 7001, Australia; <sup>5</sup>Institute for Antarctic and Southern Ocean Studies, Locked Bag 129, Hobart, Tas. 7000, Australia

### Abstract

Iron is the limiting micronutrient in the Southern Ocean and experiments have demonstrated that addition of soluble iron to surface waters results in phytoplankton blooms, particularly by large diatoms. Antarctic krill (*Euphausia superba*) eat diatoms and recycle iron in surface waters when feeding. Baleen whales eat krill, and, historically, defecation by baleen whales could have been a major mechanism for recycling iron, if whale faeces contain significant quantities of iron. We analysed the iron content in 27 samples of faeces from four species of baleen whale. Faecal iron content ( $145.9 \pm 133.7 \text{ mg kg}^{-1}$ ) is approximately ten million times that of Antarctic seawater, suggesting that it could act as a fertilizer. Furthermore, we analysed the iron content of seven krill species and of muscle tissue of two species of baleen whales; all samples had high iron levels. Using these figures, together with recent estimates of the range and biomass of krill, we calculate that the Antarctic krill population contains ~24% of the total iron in the surface waters in its range. Thus, krill can act as a long-term reservoir of iron in Antarctic surface waters, by storing the iron in their body tissue. Pre-exploitation populations of whales and krill must have stored larger quantities of iron and would have also recycled more iron in surface waters, enhancing overall ocean productivity through a positive feedback loop. Thus, allowing the great whales to recover might actually increase Southern Ocean productivity through enhancing iron levels in the surface layer.

### Correspondence:

Stephen Nicol,  
Australian Antarctic  
Division, 203  
Channel Highway,  
Kingston, Tas. 7050,  
Australia  
Tel.: 03 62323324  
Fax: 03 62 323449  
E-mail: steve.nicol@  
aad.gov.au

Received 16 Aug 2009  
Accepted 4 Mar 2010

**Keywords** Baleen whales, iron fertilization, krill, Southern Ocean

<b>Introduction</b>	<b>204</b>
<b>Methods</b>	<b>204</b>
Sampling	204
Analyses	205
Molecular determination of diet	205
Iron	205
<b>Results</b>	<b>205</b>
<b>Discussion</b>	<b>206</b>

<b>Conclusions</b>	<b>207</b>
<b>Acknowledgements</b>	<b>208</b>
<b>References</b>	<b>208</b>

---

## Introduction

The Southern Ocean is critical in the global carbon cycle and contains productive ecosystems with high conservation value (Smetacek and Nicol 2005). Iron is the limiting micronutrient in the Southern Ocean and experiments have now unequivocally demonstrated that addition of soluble iron to surface waters results in phytoplankton blooms, particularly of large diatoms (see summary by Boyd *et al.* 2007). Antarctic krill (*Euphausia superba*, Euphausiacea) graze on diatoms and, in turn, baleen whales feed on krill in the Southern Ocean. It has been suggested that, when they were more abundant, baleen whales could have been a major mechanism for recycling iron through their conversion of krill into iron-rich faeces that would be available for phytoplankton growth (Smetacek and Nicol 2005; Smetacek 2008). This theory depends, in the first instance, on whale faeces containing significant quantities of iron, something that has not yet been demonstrated. A number of studies have examined the iron content of Antarctic krill which are the chief prey of baleen whales (summarized in Palmer *et al.* 2006) and krill are rich in iron. Whether all of this iron is retained by their predators or is excreted is unknown.

Many diving marine vertebrates are rich in iron because of their elevated myoglobin levels (Kooyman 2002) and this iron must be obtained from their diet. The iron content of a number of Antarctic animals has been reported and birds and mammals contained the highest concentrations, fish contained intermediate levels and invertebrates exhibited a wide range of values (Honda *et al.* 1987). Invertebrates have varying iron contents reflecting a greater diversity of metabolic pathways when compared with vertebrates. All of the reported values for animal iron concentrations are far above the concentration of iron found in seawater, which is at the sub-nanomolar level in the open ocean (see summary in Johnson *et al.* 1997). All animals must obtain essential nutrients, such as iron, from their food. Iron is essential to phytoplankton, its major physiological role being in electron transfer processes as part of

photosynthesis and adenosine triphosphate (ATP) production (e.g. Hutchins 1995). Phytoplankton take up iron from seawater and concentrate it within the algal cell; however, iron concentrations vary significantly across cells and between communities (Twining *et al.* 2004). Animals such as krill that feed on phytoplankton must further concentrate iron in their tissue and fluids and it is this highly concentrated source of iron that provides the large quantities of this element that are required by whales, seals and penguins, many of which are obligate krill feeders. Antarctic krill have also been shown to be effective at recycling iron from phytoplankton into soluble iron by releasing it during their feeding activities (Tovar-Sanchez *et al.* 2007). For baleen whales to be an important contributor to the Southern Ocean iron cycle, they need to be able to convert large quantities of iron from a particulate form (in krill) into a diffuse form (faeces) containing a soluble fraction, which may then be available again for phytoplankton growth. To determine whether this is the case, or whether it might have been the case in the past, we measured the particulate iron content of baleen whale faeces as an indicator of the diffuse mixture of dissolved, colloidal and particulate iron in undiluted whale faeces. We also measured the iron content of whole krill and of whale muscle. The measurements have been used in conjunction with recently published figures for the range and biomass of Antarctic krill (Atkinson *et al.* 2009) to estimate the amount of iron that is contained within the flesh of whales and krill. Using historical data for the krill consumption rate of the pre-exploitation populations of baleen whales, we confirm that the krill-baleen whale system was a significant element of the iron cycle in the Southern Ocean and that even today, the populations of animals such as krill play a major role in retaining iron in the surface layer.

## Methods

### Sampling

Whale faecal samples were collected from small boats in multiple locations by trawling 0.2-mm

mesh nets through the faecal plume ejected by whales (Jarman *et al.* 2002). Whale muscle was collected from dead, stranded blue and fin whales in south-western Australia. Seven species of krill were collected by nets in various locations worldwide as part of a larger study on krill phylogeny (Jarman *et al.* 2000). All samples were preserved in >70% ethanol.

## Analyses

### Molecular determination of diet

Krill presence was confirmed in the faecal samples using a previously described polymerase chain reaction test (Jarman *et al.* 2002).

### Iron

Krill samples (stored frozen) were dried at 60 °C to constant weight. Digestion of 2–100 mg subsamples was performed in 15-mL Teflon PFA vials by addition of 1 mL of concentrated ultrapure nitric acid and 0.125 mL of ultrapure hydrogen peroxide and heated at 125 °C for 8 h. Identical procedures were applied to blanks ( $n = 6$ ) and to two certified referenced materials ( $n = 5$ ) (DORM-3 fish protein; National Research Council, Ottawa, Canada; and NIST 1566a oyster tissue; National Institute of Standards and Technology, Gaithersburg, Maryland, USA). Certified materials, blanks and samples were resuspended in 10–100 mL of 10% nitric acid and analysed by inductively coupled

plasma mass spectrometry, following Cullen and Sherrell (1999) and Townsend (2000). Iron content in the blanks represented <0.1% of the sample. Reference data compared well with certified values for both DORM-3 (measured:  $322 \pm 42 \text{ mg kg}^{-1}$ , certified:  $347 \pm 20 \text{ mg kg}^{-1}$ ) and Oyster 1566a (measured:  $478 \pm 12 \text{ mg kg}^{-1}$ , certified  $539 \pm 15 \text{ mg kg}^{-1}$ ), representing recoveries of 93 and 89% respectively. Typical precision between replicate analysis of identical digest solutions was <1%, and between different subsamples of the whale muscle was 21–30%.

## Results

The mean faecal iron content from the four species of baleen whales examined was  $166.6 \pm 155.2 \text{ mg kg}^{-1}$  dry weight (Table 1). This concentration is over ten million times that of Antarctic seawater ( $\sim 0.2 \text{ nmol L}^{-1}$  or  $\sim 10 \text{ ng kg}^{-1}$ ; Bowie *et al.* 2001), suggesting that it should act as an effective fertilizer. All sampled whale faeces tested positive for krill. Samples of fin whale faeces were studied in detail by clone library analysis, which determined that krill was the major food item, accounting for all 15 food sequences identified (Jarman *et al.* 2004). The other samples were tested by quantitative PCR that produced signal strengths per ng of total DNA template of at least 65% of the signal strength per ng seen in the fin whale samples. Although quantification of dietary items by DNA-

**Table 1** Samples analysed for iron content.

Sample type	Species	No. of samples examined	Iron concentration ( $\text{mg kg}^{-1}$ dry weight)
Whale faeces (Balaenopteridae)	Blue, <i>Balaenoptera musculus</i>	15	$172.4 \pm 114.1$
	Pygmy blue, <i>Balaenoptera musculus brevipinna</i>	7	$63.4 \pm 17.7$
	Humpback, <i>Megaptera novaeangliae</i>	2	118.6
	Fin, <i>Balaenoptera physalus</i>	2	237.4
Whole krill (Euphausiacea)	Antarctic krill, <i>Euphausia superba</i>	(5)	174.3
	<i>Pseudeuphausia latifrons</i>	(5)	151.1
	<i>Nyctiphanes australis</i>	(5)	91.4
	<i>Euphausia pacifica</i>	(5)	62.1
	<i>Euphausia similis</i>	(5)	36.5
	<i>Euphausia krohnii</i>	(5)	34.2
	<i>Meganyctiphanes norvegica</i>	(10)	$12.0 \pm 3.3$
Whale muscle	Blue, <i>Balaenoptera musculus</i>	1	58.3
	Fin, <i>Balaenoptera physalus</i>	1	215.7
	Mean		137.0

Whale faecal samples were analysed individually, krill samples were batched before analysis and the number of animals used is shown in brackets.

based methods is not precise or simple, these results indicate that krill were a major dietary item for all the samples tested for iron concentration.

The mean iron content of the seven species of krill examined, including some of those species detectable in faecal samples, was between 12 and 174 mg kg<sup>-1</sup> dry weight (Table 1), and the average iron content of the muscle tissue of blue and fin whales was 137 mg kg<sup>-1</sup> dry weight (Table 1).

## Discussion

The faeces of baleen whales contain large quantities of iron, comparable in concentration with that found in the tissues of vertebrates and krill. This confirms the suggestion put forward by Smetacek (2008) that defecation by baleen whales should have a fertilizing effect by releasing iron back into the surface layer. The measured iron content of Antarctic krill agrees with published values, which range from 5.7–212 mg kg<sup>-1</sup> (summarized in Palmer *et al.* 2006). The iron content of whale muscle also accords with published values of the iron content of diving air-breathing vertebrates: minke whale (*Balaenoptera acutorostrata*, Balaenidae) muscle 35.5 µg g<sup>-1</sup> wet weight, Adelle penguin (*Pygoscelis adeliae*, Pygoscelidae) 143 µg g<sup>-1</sup> wet wt. and Weddell seal (*Leptonychotes weddellii*, Phocidae) 252 µg g<sup>-1</sup> wet wt. (Honda *et al.* 1987). Thus, the iron tied up in the bodies of large animals in the Southern Ocean could be significant in terms of the cycle of this element in the surface layer.

Iron has a shorter residence time in the Southern Ocean than other essential nutrients (Smetacek 2008), so any mechanism that increases the persistence of bioavailable iron in the surface layer will tend to enhance productivity. As krill are so abundant in the Southern Ocean and because they have a high iron content, they could serve as an effective reservoir of iron in the surface layer. Krill are long-lived and they are active swimmers, so they are able to maintain essential nutrients in the surface layer where as smaller passive particles tend to sink below the thermocline. To estimate the size of the iron reservoir in the krill population, we used the most recent estimates of Southern Ocean krill biomass: 379 million tonnes (Atkinson *et al.* 2009). By simple multiplication, using an iron content of 174.3 mg kg<sup>-1</sup> and assuming that the dry weight of krill is 23% of the wet weight (Nicol *et al.* 1992), we estimate the amount of iron present in the current krill population to be ~15 000 tonnes.

Antarctic krill are concentrated in the surface 200 m in an area of 19 million km<sup>2</sup> (Atkinson *et al.* 2009), thus the water volume occupied by krill is 3.8 × 10<sup>6</sup> km<sup>3</sup>. The concentration of iron in Antarctic seawater not associated with metazoan animals (dissolved plus particulate) is typically ~0.3 nmol L<sup>-1</sup> (Bowie *et al.* 2009); therefore, there is ~63 000 tonnes of iron in the volume of seawater occupied by the krill population. Thus, the population of krill contains ~24% of the iron in their habitat. Krill also release iron into the water when they are feeding and measurements of recycling of iron by krill suggest that they can release 22–689 nmol iron g dry weight<sup>-1</sup> h<sup>-1</sup>, equivalent to 0.2 to 4.3 nmol Fe L<sup>-1</sup> day<sup>-1</sup> and can be a significant player in the pelagic iron cycle (Tovar-Sanchez *et al.* 2007). So the role of krill may be keeping iron in suspension for long periods and releasing this iron slowly through excretion and through feeding activities.

There are suggestions that the current population of krill may be only 20% of its pre-1980s size (Atkinson *et al.* 2004). A larger krill population would have stored a correspondingly larger amount of iron and would also have recycled more iron into the surface layer. If the population of krill in the early 20th century was really five times that of today, there would have to have been more iron in the surface layer of the Southern Ocean, even if much of it was tied up in krill tissue. As iron is limiting primary production in the Southern Ocean, a much larger krill population would imply that there was greater primary production to support it (Smetacek 2008).

The current biomass of baleen whales in the Southern Ocean is uncertain, but the pre-exploitation biomass was 34.2–41.7 million tonnes (Mori and Butterworth 2006). The mean iron content of whale muscle from our measurements is 137.0 mg iron kg<sup>-1</sup> dry weight. Whale muscle is approximately 50% of the wet weight of a baleen whale and muscle contains ~75% water (Brodie 1975). Using a mean value for the pre-exploitation whale population size (38 million tonnes) and the mean iron content that we measured (1.37 × 10<sup>-3</sup> mg Fe kg<sup>-1</sup>), then the historical whale population would have contained approximately 650 tonnes of iron. While this figure is only 1% of the estimated iron content in the seawater in the whale feeding grounds, the major effect of whales would be in their role of converting unavailable iron bound up in krill tissue into more bioavailable iron in faeces.

The pre-exploitation baleen whale population in the Southern Ocean was dominated by fully grown adults and during their seasonal feeding migrations they would be largely producing blubber rather than muscle tissue, so most of the iron in their diet would have been expelled as faeces (Smetacek 2008). Baleen whale faeces are released as a slurry, which disperses rapidly in the surface layer. It has been estimated that whales consumed some 190 million tonnes of krill per year (Laws 1977; Mori and Butterworth 2006), thus they converted some 7600 tonnes of iron in krill into iron-rich faeces every year, some 12% of our estimate of the current iron content of the surface layer. Smetacek (2008) considered the figure of 190 million tonnes of krill a year consumed by baleen whales to be a conservative figure, so the contribution to recycling by whales could be even higher. Thus, whales would have been part of a positive feedback loop that maintained primary productivity by efficiently recycling iron in the surface waters. Larger populations of whales would have led to enhanced primary productivity and this larger food source would have potentially supported bigger krill populations.

There was speculation that the removal of the great whales from the Southern Ocean would lead to a 'krill surplus' and that this excess krill would gradually be taken up by populations of other krill dependent predators such as seabirds and seals (Laws 1977). In fact, there is little direct or indirect evidence that the krill population boomed following commercial whaling and there are suggestions that the krill population was larger in the 1930s than it is now (Atkinson *et al.* 2004). There are few examples of krill predators that experienced increases in population sizes as a result of any increase in food supply (Mori and Butterworth 2006; Smetacek 2008). There has also been no consistent trend in the population sizes of major krill predators; some have declined, some have remained unchanged and some have increased (Croxall 1992; Fraser *et al.* 1992; Weimerskirch *et al.* 2003). If the krill-whale system is as important in the Southern Ocean as our simple calculations seem to suggest, then removal of one key element of the system (baleen whales) would detrimentally affect overall ecosystem productivity. Some species of baleen whales are making quite rapid recoveries in the Southern Ocean (International Whaling Commission (IWC) 2003) and it will be instructive to monitor whether the unhindered recovery of these

populations will have a positive or negative long-term effect on krill populations.

Krill are long-lived animals and thus they can act as a mechanism for retaining iron in the surface layer of the Southern Ocean, particularly during the winter months. While baleen whales migrate to their reproductive grounds, krill remain in Antarctic waters and act as a swimming iron reservoir during winter when passively sinking particles such as phytoplankton or detritus become lost to the ocean depths. Other actively swimming Southern Ocean herbivores may also play a role in maintaining iron in surface waters. Measurements of the elemental composition of copepods suggest that these highly abundant herbivores are also rich in iron (Honda *et al.* 1987) and some species of baleen whales (right, sei) are known to be primarily copepod feeders, particularly in the subantarctic zone. These observations suggest that the animal component of the iron cycle in the oceans has been overlooked.

There is a growing literature that is beginning to suggest that the role of larger animals in structuring marine ecosystems has been greatly underestimated (Seibel and Dierssen 2009). Fish have recently been shown to be significant players in the calcium carbonate cycle of the oceans (Wilson *et al.* 2009). Krill, jellyfish and other vertically migrating animals have been shown to disrupt the physical structure of the upper ocean through the turbulent mixing associated with their diurnal vertical movements (Huntley and Zhou 2004; Dewar *et al.* 2006; Kunze *et al.* 2006; Kajita and Dabri 2009). These effects of animals on ocean chemistry and structure would not act in isolation, so large animals can act at several levels in the ecosystem simultaneously – neither simply top-down, or bottom-up. The removal of large predators from marine ecosystems thus may well affect not only foodweb structure but also the seawater chemistry and physics, and thus negatively impact on the underlying primary production. A range of studies have documented the higher level of diversity and productivity of marine ecosystems in the presence of large animals (see Roberts 2007), which seems to point to the positive ecological effect of larger animals.

## Conclusions

Our results indicate that one element of the hypothesis put forward by Smetacek (2008) to account for the productivity of the Southern Ocean is plausible – whale faeces do contain considerable

amounts of iron and they should act as a fertilizer. Future studies will need to focus on the buoyancy of the faeces and the bioavailability of the faecal iron to demonstrate the effectiveness of this fertilization. Our simple calculations suggest that whales and krill can play a major role in the iron cycle in the Southern Ocean by retaining iron and releasing this important micronutrient into the surface layer. The effect of the krill-whale ecosystem on iron recycling would have been even more significant in the pre-exploitation era. Thus, allowing the great whales to recover might actually increase the overall productivity of the Southern Ocean.

### Acknowledgements

This study was developed from some original ideas published by Victor Smetacek whose intellectual underpinning is gratefully acknowledged. This work was supported by the Australian Government's Cooperative Research Centres Programme through the Antarctic Climate and Ecosystem Cooperative Research Centre, by the Australian Antarctic Division and by the Australian Marine Mammal Centre. We thank Ashley Townsend for analytical support. No whales were killed in the pursuit of this research.

### References

- Atkinson, A., Siegel, V., Pakhomov, E. and Rothery, P. (2004) Long-term decline in krill stock and increase in slaps within the southern ocean. *Nature* **432**, 100–103.
- Atkinson, A., Siegel, V., Pakhomov, E.A., Jessopp, M.J. and Loeb, V. (2009) A re-appraisal of the total biomass and annual production of Antarctic krill. *Deep-Sea Research I* **56**, 727–740.
- Bowie, A.R., Maldonado, M.T., Frew, R.D. *et al.* (2001) The fate of added iron during a mesoscale fertilisation experiment in the Southern Ocean. *Deep-Sea Research II* **48**, 2703–2743.
- Bowie, A.R., Lannuzel, D., Remenyi, T.A. *et al.* (2009) Biogeochemical iron budgets of the Southern Ocean south of Australia: Decoupling of iron and nutrient cycles in the subantarctic zone by the summertime supply. *Global Biogeochemical Cycles* **23**, GB4034, doi: 10.1029/2009GB003500.
- Boyd, P.W., Jickells, T., Law, C.S. *et al.* (2007) Mesoscale iron enrichment experiments 1993–2005: synthesis and future directions. *Science* **315**, 612–617.
- Brodie, P.F. (1975) Cetacean energetics, an overview of intraspecific size variation. *Ecology* **56**, 152–161.
- Croxall, J.P. (1992) Southern Ocean environmental changes: effects on seabird, seal and whale populations. *Philosophical Transactions of the Royal Society of London B* **358**, 319–328.
- Cullen, J.T. and Sherrell, R.M. (1999) Techniques for determination of trace metals in small samples of size fractionated particulate matter: phytoplankton metals off central California. *Marine Chemistry* **67**, 233–247.
- Dewar, W.K., Bingham, R.J., Iverson, R.L., Nowaceki, D.P., St Laurent, L.C. and Wiebe, P.H. (2006) Does the marine biosphere mix the ocean? *Journal of Marine Research* **64**, 541–561.
- Fraser, W.R., Trivelpiece, W.Z., Ainley, D.G. and Trivelpiece, S.G. (1992) Increases in Antarctic penguin populations-reduced competition with whales or a loss of sea ice due to environmental warming. *Polar Biology* **11**, 525–531.
- Honda, K., Yoshiyuki, Y. and Tatsukawa, R. (1987) Distribution of heavy metals in Antarctic Marine Ecosystem. *Proceedings of the National Institute Polar Research Symposium on Polar Biology* **1**, 184–197.
- Huntley, M. and Zhou, M. (2004) Influence of animals on turbulence in the sea. *Marine Ecology Progress Series* **273**, 65–79.
- Hutchins, D.A. (1995) Iron and the marine phytoplankton community. In: *Progress in Phycological Research* (eds F.E. Round and D.J. Chapman). Biopress Ltd, New York, pp. 1–48.
- International Whaling Commission (IWC) (2003) Report of the Sub-Committee on the comprehensive assessment of whale stocks – in-depth assessments. *Journal of Cetacean Research and Management* **5**(Suppl.), 248–292.
- Jarman, S.N., Nicol, S., Elliot, N.G. and McMinn, A. (2000) 28S rDNA evolution in the Eumalacostraca and the phylogenetic position of krill. *Molecular Phylogeny and Evolution* **17**, 26–36.
- Jarman, S.N., Gales, N.J., Tierney, M., Gill, P.C. and Elliott, N.G. (2002) A DNA-based method for identification of krill species and its application to analysing the diet of marine vertebrate predators. *Molecular Ecology* **11**, 2679–2690.
- Jarman, S.N., Deagle, B.E. and Gales, N.J. (2004) Group-specific polymerase chain reaction for DNA-based analysis of species diversity and identity in dietary samples. *Molecular Ecology* **13**, 1313–1322.
- Johnson, K.S., Gordon, R.M. and Coale, K.H. (1997) What controls dissolved iron concentrations in the world ocean? *Marine Chemistry* **57**, 137–161.
- Kajita, K. and Dabri, J.O. (2009) A viscosity enhanced mechanism for biogenic ocean mixing. *Nature* **460**, 624–626.
- Kooyman, G.L. (2002) Diving physiology. In: *Encyclopaedia of Marine Mammals* (eds W.F. Perrin, B. Wursig and J.G.M. Thewissen). Academic Press, San Diego, pp. 339–344.
- Kunze, E., Dower, J.F., Beveridge, I., Dewey, R. and Bartlett, K.P. (2006) Observations of biologically generated turbulence in a coastal inlet. *Science* **313**, 1768–1770.

- Laws, R.M. (1977) Seals and whales of the Southern Ocean. *Philosophical Transactions of the Royal Society of London B* **279**, 81–96.
- Mori, M. and Butterworth, D.S. (2006) A first step towards modelling the krill–predator dynamics of the Antarctic ecosystem. *CCAMLR Science* **13**, 217–277.
- Nicol, S., Stolp, M. and Nordstrom, O. (1992) Changes in the gross biochemistry and mineral content accompanying the moult cycle in the Antarctic krill (*Euphausia superba* Dana). *Marine Biology* **113**, 201–209.
- Palmer, A.S., Snape, I., Stark, J.S., Johnstone, G.L. and Townsend, A.T. (2006) Baseline metal concentrations in *Paramoera walkeri* from East Antarctica. *Marine Pollution Bulletin* **52**, 1441–1449.
- Roberts, C. (2007) *The Unnatural History of the Sea*. Island Press, Washington, D.C, USA, 457 pp.
- Seibel, B.A. and Dierssen, H.M. (2009) Animal function at the heart (and gut) of oceanography. *Science* **323**, 343–344.
- Smetacek, V. (2008) Are declining Antarctic krill stocks a result of global warming or the decimation of the whales? In: *The Impact of Global Warming on Polar Ecosystems* (ed. C. Duarte). Fundacion BBVA, Spain, pp. 46–83.
- Smetacek, V. and Nicol, S. (2005) Polar ocean ecosystems in a changing world. *Nature* **437**, 362–368.
- Tovar-Sanchez, A., Duarte, C.M., Hernández-León, S. and Sañudo-Wilhelmy, S.A. (2007) Krill as a central node for iron cycling in the Southern Ocean. *Geophysical Research Letters* **34**, L11601, doi: 10.1029/2006GL029096.
- Townsend, A.T. (2000) The accurate determination of the first row transition metals in water, urine, plant, tissue and rock samples by sector field ICP-MS. *Journal of Analytical Atomic Spectrometry* **15**, 307–314.
- Twining, B.S., Baines, S.B., Fisher, N.S. and Landry, M.R. (2004) Cellular iron contents of plankton during the Southern Ocean Iron Experiment (SOFEX). *Deep-Sea Research I* **51**, 1827–1850.
- Weimerskirch, H., Inchausti, P., Guinet, C. and Barbraud, C. (2003) Trends in bird and seal populations as indicators of a system shift in the Southern Ocean. *Antarctic Science* **15**, 249–256.
- Wilson, R.W., Millero, F.J., Taylor, J.R. *et al.* (2009) Contribution of fish to the marine inorganic carbon cycle. *Science* **323**, 359–362.