



Pelagic Iron Recycling in the Southern Ocean: Exploring the Contribution of Marine Animals

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The availability of iron controls primary productivity in large areas of the Southern Ocean. Iron is largely supplied via atmospheric dust deposition, melting ice, the weathering of shelf sediments, upwelling, sediment resuspension, mixing (deep water, biogenic, and vertical mixing) and hydrothermal vents with varying degrees of temporal and spatial importance. However, large areas of the Southern Ocean are remote from these sources, leading to regions of low primary productivity. Recent studies suggest that recycling of iron by animals in the surface layer could enhance primary productivity in the Southern Ocean. The aim of this review is to provide a quantitative and qualitative assessment of the current literature on pelagic iron recycling by marine animals in the Southern Ocean and highlight the next steps forward in quantifying the retention and recycling of iron by higher trophic levels in the Southern Ocean. Phytoplankton utilize the iron in seawater to meet their metabolic demand. Through grazing, pelagic herbivores transfer the iron in phytoplankton cells into their body tissues and organs. Herbivores can recycle iron through inefficient feeding behavior that release iron into the water before ingestion, and through the release of fecal pellets. The iron stored within herbivores is transferred to higher trophic levels when they are consumed. When predators consume iron beyond their metabolic demand it is either excreted or defecated. Waste products from pelagic vertebrates can thus contain high concentrations of iron which may be in a form that is available to phytoplankton. Bioavailability of fecal iron for phytoplankton growth is influenced by a combination of the size of the fecal particle, presence of organic ligands, the oxidation state of the iron, as well as biological (e.g., remineralization, coprochaly, coprorhexy, and coprophagy) and physical (e.g., dissolution, fragmentation) processes that lead to the degradation and release of fecal iron. The flux of dissolved iron from pelagic recycling is comparable to other sources in the region such as atmospheric dust, vertical diffusivity, vertical flux, lateral flux and upwelling, but lower than sea ice, icebergs, sediment resuspension, and deep winter mixing. The temporal and seasonal importance of these various factors requires further examination.

Keywords: biological carbon pump, iron, carbon, Southern Ocean, biological recycling

INTRODUCTION

The ocean is a major sink of anthropogenic carbon dioxide (CO₂) which occurs through a combination of the physical and the biological carbon pumps. Cold surface seawaters enhance the solubility of atmospheric CO₂ into the ocean. In the Southern Ocean, the cold seawater south of the Polar Front mixes with the warmer waters in the sub-Antarctic region and sink, transporting the CO₂ to the deep ocean and thereby removing it from the atmosphere (Khatiwala et al., 2009, 2013). The fixation of CO₂ into deep-sinking particulate organic carbon (POC), known as the biological pump, can globally remove an estimated 10×10^{12} kg of carbon from the pelagic zone each year (Falkowski et al., 1998; Buesseler and Boyd, 2009; Passow and Carlson, 2012).

Our understanding of the processes that regulate the solubility of CO₂ in seawater is relatively well constrained. In contrast, the biological carbon pump is less well understood. This is because many of the mechanisms underpinning key process such as the retention, uptake, recycling, remineralization and export of nutrients such as iron (Fe) and carbon are spatially and temporally variable (Boyd et al., 2017). Primary production depends on the availability of light, CO₂ and the presence of a wide range of nutrients such as: Fe and manganese (Mn) for carbon fixation, zinc (Zn), cadmium (Cd), and cobalt (Co) for CO₂ acquisition, Zn and Cd for silica uptake by large diatoms' Co and Zn as calcifiers, Fe for nitrogen (N₂) fixation, copper (Cu) and Fe for nitrification, denitrification and organic N utilization, Zn for organic phosphorus (P) utilization, Fe for synthesis of photopigments, and Cu for methane oxidation (Morel and Price, 2003; Morel et al., 2003). However, the scarcity of some micronutrients such as Fe can limit primary productivity across large areas of the ocean, thereby reducing the efficiency of the biological carbon pump (Martin, 1990; Martin et al., 1990; Bowie et al., 2001; Blain et al., 2007; Boyd et al., 2007, 2017). The aim of this review is to qualitatively and quantitatively assess the role of marine animals such as herbivores and their predators in recycling Fe in the Fe-limited Southern Ocean and propose key future steps in examining the role of higher trophic levels on the marine Fe and carbon cycle.

Sources of Iron to Southern Ocean Surface Waters

The predominant supply of Fe into the ocean has been considered to be from the deposition of atmospheric dust from the surrounding continents (Boyd et al., 2004; Jickells et al., 2005; Cassar et al., 2007). However, the importance of atmospheric Fe deposition is regionally variable. For example, atmospheric Fe blown from the Sahara Desert is a major source of Fe in the Atlantic Ocean and Mediterranean Sea (Guieu et al., 2002; Sarthou et al., 2003). In contrast, atmospheric dust is a less important source of Fe in the Southern Ocean, with an estimated dissolved Fe contribution of $0.00027\text{--}0.05 \mu\text{mol m}^{-2} \text{day}^{-1}$ (Table 1). This is because Antarctica is ice-covered, which greatly reduces access to sources of dust, and circumpolar winds and currents isolate much of the Southern Ocean from the other continents further north.

TABLE 1 | Flux of dissolved iron ($\mu\text{mol m}^{-2} \text{day}^{-1}$) from various sources in the Southern Ocean.

Source	Flux ($\mu\text{mol m}^{-2} \text{day}^{-1}$)	References
Blue whales and krill	0.03	Ratnarajah et al., 2016a
Antarctic krill	0.002–0.076	Tovar-Sanchez et al., 2007; Schmidt et al., 2011
Atmospheric dust	0.00027–0.05	Duce and Tindale, 1991; Lefèvre and Watson, 1999; Fung et al., 2000; Bowie et al., 2001, 2015; Mahowald et al., 2005; Wagener et al., 2008; Lancelot et al., 2009
Sea ice	0.3	Lannuzel et al., 2007
Icebergs	0.19	Lancelot et al., 2009
Sediment resuspension	0.1–2	Moore et al., 2004; Blain et al., 2007; Dulaiova et al., 2009
Vertical diffusivity	0.007–0.093	Boyd et al., 2005; Bowie et al., 2009, 2015
Vertical flux	0.004–0.031	Blain et al., 2007; Charette et al., 2007
Lateral flux	0.064–0.39	Charette et al., 2007
Upwelling	0.02–0.33	de Baar et al., 1995; Watson, 2001; Lannuzel et al., 2007; Bowie et al., 2015
Deep winter mixing	0.02–0.09	Tagliabue et al., 2014

More than 40% of the Southern Ocean is seasonally covered by sea ice, which is a significant source of Fe during spring melt, stimulating much of the productivity observed from satellites. Sea ice forms as the seawater temperature drops below -1.86°C , whilst incorporating the Fe from seawater into the ice. The spring-time melting of sea ice (Sedwick and Di Tullio, 1997; Lannuzel et al., 2007), ice shelves (Herraiz-Borreguero et al., 2016), and icebergs (Smith et al., 2007; Lancelot et al., 2009; Lin et al., 2011; Duprat et al., 2016) release the trapped Fe into the surface waters. Other sources of Fe can include: hydrothermal vents (Tagliabue et al., 2010; Klunder et al., 2011), upwelling (de Baar et al., 1995; Watson, 2001), deep winter mixing (Tagliabue et al., 2014), biogenic mixing (Katija and Dabiri, 2009; Katija, 2012), vertical mixing (Webb and Sugihara, 2001; Cisewski et al., 2005; Frants et al., 2013), the weathering of shelf sediments (Sedwick et al., 2008; Bowie et al., 2009), sediment resuspension (Moore et al., 2004; Blain et al., 2007; Dulaiova et al., 2009) and pelagic recycling (Tovar-Sanchez et al., 2007; Ortega-Retuerta et al., 2009; Schmidt et al., 2011, 2016; Lehette et al., 2012; Ratnarajah et al., 2014, 2016a,b, 2017; Wing et al., 2014, 2017; Shatova et al., 2016; Laglera et al., 2017).

Using a combination of models and point-source observations, studies have attempted to estimate the flux of dissolved Fe from these various sources into the Southern Ocean (Table 1). These flux estimates are highly localized, do not represent a constant daily flux, and the calculated upper limits will only be realized close to their respective sources. Therefore, localized flux estimates are not easily extrapolated to basin scales. However, as a localized source, the flux of fecal derived dissolved Fe from baleen whales and Antarctic krill are comparable to other sources in the region such as atmospheric dust, vertical

diffusivity, vertical flux, lateral flux and upwelling, but lower than sea ice, icebergs, sediment resuspension, and deep winter mixing (Table 1).

Overview of Pelagic Iron Recycling by Marine Animals

Uptake of Fe by phytoplankton occurs within the euphotic zone over spring and summer (Figure 1). Microzooplankton such as flagellates and ciliates graze on phytoplankton in the euphotic zone (Safi et al., 2007; Pearce et al., 2011; Yang E. J. et al., 2016), whilst invertebrate herbivores such as krill, salps, copepods actively graze on phytoplankton and microzooplankton (Schmidt et al., 2014; Dupuy et al., 2016; Schmidt and Atkinson, 2016; Yang G. et al., 2016). Some of the nutrients ingested by herbivores is retained to satisfy their metabolic demands (e.g., Cu for respiratory pigment in crustaceans; Spicer and Saborowski, 2010, ammonia/ammonium for neutral buoyancy in diapausing calanoid copepods; Sartoris et al., 2010). Herbivores recycle nutrients during feeding through inefficiencies in the feeding behavior (sloppy feeding) and via the excretion/defecation of excess nutrients.

The sloppy feeding during grazing by copepods and microzooplankton have been shown to release Fe and Fe-binding ligands into the water column (Sato et al., 2007; Sarthou et al., 2008; Laglera et al., 2017). This Fe might be available to primary producers (Figure 1). Excess nutrients beyond metabolic demand of zooplankton is ejected from their body by excretion or defecation (Tovar-Sanchez et al., 2007; Ortega-Retuerta et al., 2009; Ruiz-Halpern et al., 2011; Schmidt et al., 2011, 2016; Lehette et al., 2012; Ratnarajah et al., 2016b). For instance, Antarctic krill consume phytoplankton and process the ingested Fe within their digestive organs and muscle (Nicol et al., 2010; Schmidt et al., 2011, 2016; Ratnarajah et al., 2016b). Only two studies have measured the Fe concentrations in krill digestive organs, reporting a range from 13 to 2,783 mg kg⁻¹ dry weight, with the variability likely driven by a combination of seasonal and regional differences in sampling, reflecting differences in the quantity and quality of their diet (Ratnarajah et al., 2016b; Schmidt et al., 2016).

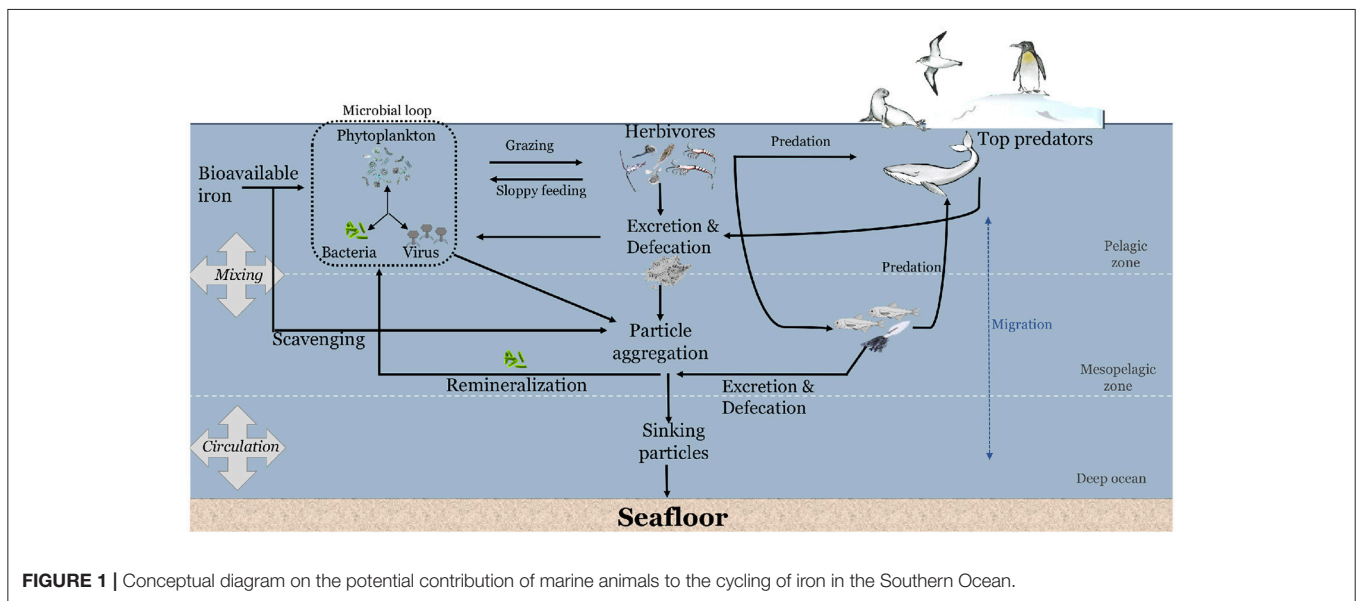
A fraction of the Fe ingested by krill is retained in their muscle, with excess Fe being released in their fecal pellets (Nicol et al., 2010; Schmidt et al., 2011, 2016; Ratnarajah et al., 2016b). Additionally, excretion by Antarctic krill can release a portion of their ingested Fe. Experiments have suggested that krill excretion could increase total Fe concentrations in the seawater by 0.2–4.3 nM Fe L⁻¹ d⁻¹ (Tovar-Sanchez et al., 2007). Other Southern Ocean herbivores will have different effects on Fe cycling. For example, salp (*Salpa thompsoni*) fecal pellets appear to be retained in the upper 300 m of the water. Although these pellets contain high levels of Fe, they are highly refractory and do not release dissolved Fe via physicochemical pathways (Cabanes et al., 2017). Therefore, grazing by salps may lead to the depletion of Fe from surface seawater, with an estimated dissolved Fe export flux of 11.3 nmol Fe m⁻² d⁻¹ at 300 m (Cabanes et al., 2017). In addition, the large populations of pelagic herbivores in the Southern Ocean contain a significant amount of Fe in their bodies (Nicol et al., 2010). This Fe is unavailable to phytoplankton but

can be released by excretion and defecation after the herbivores have been consumed by carnivores. Some herbivores are long-lived and can store Fe in their bodies between seasons and because they can swim, they retain this Fe in the pelagic zone.

The varying density and sinking rate of the fecal pellets of herbivores is a function of their size and shape and this results in species-specific differences in pellet retention in surface waters vs. export to deeper waters (Bruland and Silver, 1981; Turner, 2002, 2015). Although physicochemical processes may not degrade fecal pellets, biological processes such as coprophagy (fragmentation of pellets), coprophagy (ingestion of pellets) and coprochaly (loosening of pellets) by other pelagic species, and bacterial degradation via the free-living *in situ* bacterial community or internal gut bacteria could remineralize the fecal pellets and may constitute an important component of nutrient recycling within the mixed layer (see reviews by Turner, 2002, 2015).

In addition, to their role in biological degradation processes, many herbivorous organisms undertake seasonal and diurnal vertical migration from the euphotic zone into deep waters which may redistribute nutrients. The deep ocean is richer in Fe than the surface waters (Bucciarelli et al., 2001; Boyd and Ellwood, 2010; Tagliabue et al., 2014). Such migratory movements have the potential to influence the transport of nutrients from the surface to the deep ocean, and vice versa (Smetacek and Nicol, 2005; Smetacek, 2008; Schmidt et al., 2011). For example, although most of the biomass of Antarctic krill is located within the upper 150 m of the water column (Demer and Hewitt, 1995; Lascara et al., 1999), Antarctic krill have been shown to actively feed at the seabed (Clarke and Tyler, 2008), thus influencing the vertical transfer of “new” Fe from the seafloor (Schmidt et al., 2011). However, vertically migrating herbivores would only influence the transfer of Fe if they ingest Fe at depth and release excretory products within the euphotic zone. Conversely, vertical migration by animals transfer carbon, Fe and other nutrients to the deep ocean and this may remain there if the animals are consumed or if the nutrients are released at depth (Schnitzer and Steinberg, 2002; Street and Payton, 2005). Vertical migration by animals can therefore either contribute to the enhancement or depletion of nutrient concentrations in the surface layer, depending on a range of temporal and spatial variables as well as the mix of species present.

The larger carnivores (e.g., seabirds, seals, whales etc.) consume the pelagic herbivores and some of the smaller carnivores, thereby transferring the nutrients from one trophic level onto the next. What happens next is dependent on the nature of the larger carnivore. Air breathing carnivores are linked to the surface so they release nutrients in the euphotic zone, or to their land-based colonies in the case of seals and seabirds. Some vertebrates and squid feed at great depth and can release their accumulated nutrients near the surface. This group of animals inexorably draws nutrients closer to the surface. Such recycling of excess nutrients that were ingested but not assimilated has been demonstrated in seabirds (Wing et al., 2014, 2017; Shatova et al., 2016), as well as land and pelagic dwelling marine mammals (Smetacek and Nicol, 2005; Nicol et al., 2010; Ratnarajah et al., 2014, 2017; Wing et al., 2014). Vertebrate fecal material has been



linked to Fe enrichments within their local environment and this can stimulate phytoplankton growth (Shatova et al., 2016). Mesopelagic predators, such as squid and some fish species, on the other hand, spend most of their time at depth and only approach the euphotic zone sporadically. This group of animals may absorb their nutrients near the surface and draw them down to depth, however, no published studies have examined the relative contribution of mesopelagic predators to the cycling and/or export of Fe in the water column. Once again, the nature of the animal populations, the time of year and the location will all affect the magnitude and direction of nutrient cycling.

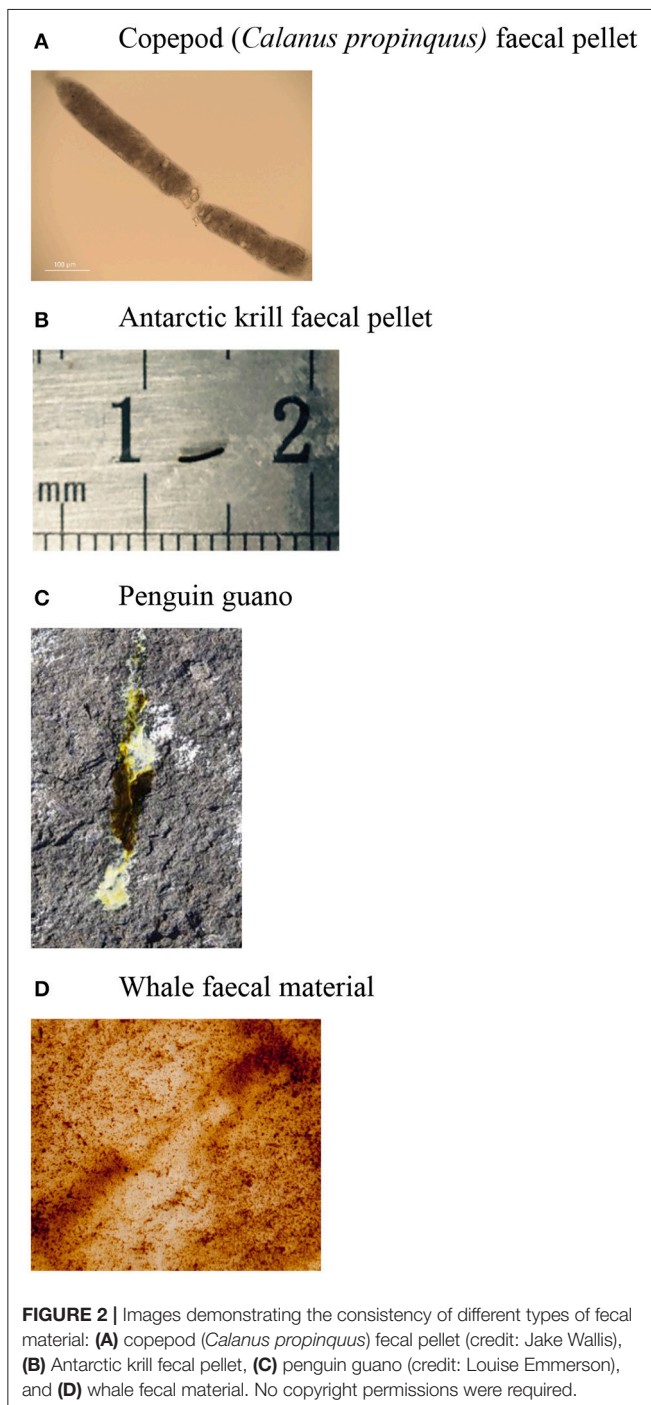
Iron Bioavailability

Not all Fe present in seawater is considered bioavailable. Bioavailability of Fe is influenced by the size and nature of the Fe particles, the complexation of certain forms of dissolved Fe by organic ligands, and by the oxidation state, with different phytoplankton classes able to access different chelated Fe species. The size fractionation between dissolved and particulate (operational cut-off of 0.2 or 0.4 μm) phases is the most commonly used as an approximation of element bioavailability, with dissolved Fe being considered as the most accessible form for biological uptake despite the particulate Fe fraction being the dominant pool of total Fe in the water column (de Baar and de Jong, 2001; Boyd and Ellwood, 2010; Lannuzel et al., 2011). The dissolved Fe pool can be further partitioned into two smaller fractions, soluble Fe (<0.02 μm) and colloidal Fe (between 0.02 μm and 0.2 or 0.4 μm). The relative importance of these fractions is uncertain. Wu et al. (2001) demonstrated that the soluble fraction may be more bioavailable than the more chemically dynamic colloidal fraction, while Honeyman and Santschi (1989) demonstrated that the colloidal fraction could aggregate into larger particles and settle from the water column.

Fecal material released from marine animals span the dissolved to particulate size continuum (Figure 2). Some

animals, such as copepods and krill, release fecal pellets bound within a peritrophic membrane, others defecate fecal material with a pulp-like consistency (e.g., seabird guano), or a liquid slurry at/close to the sea surface (e.g., whales) (Figure 2). Laboratory dissolution experiments of whale fecal material using natural seawater suggests that Fe continues to leach from the fecal particles over a 12 h time period (Ratnarajah et al., 2017). Despite the high Fe concentrations measured in krill (Schmidt et al., 2011, 2016; Ratnarajah et al., 2016b), seabird (Wing et al., 2014, 2017; Shatova et al., 2016) and whale (Nicol et al., 2010; Ratnarajah et al., 2014, 2017; Wing et al., 2014), fecal material bioavailability of the fecal Fe will depend on the size of the fecal particle, and/or the dissolution of fecal particles over time. In comparison, salp fecal pellets contain high concentrations of Fe, but the pellets are highly refractory (Cabanès et al., 2017). The peritrophic membrane may prevent the degradation of fecal pellets (Turner, 2002). Consequently, the consistency of fecal material will influence the potential bioavailability, where dissolved material may be favored over particulate material, however the dissolution of the particulate fraction in seawater, and microbial degradation may render this fraction bioavailable for uptake.

Complexation by some organic ligands also enhances the bioavailability of Fe for phytoplankton uptake (Gledhill and van den Berg, 1994; Boye et al., 2001, 2010; Hunter and Boyd, 2007; Hassler and Schoemann, 2009; Hassler et al., 2011a,b, 2012; Strzepak et al., 2011; Lannuzel et al., 2015). Organic ligands are molecules that can be excreted by the biota (e.g., siderophores are produced by bacteria as a response to Fe stress, Gledhill et al., 2004; Mawji et al., 2011), or during zooplankton grazing (Sato et al., 2007; Sarthou et al., 2008), that bind with trace metals forming stable complexes. More than 99% of the dissolved Fe in seawater is now known to be associated with strong organic ligands (Hassler et al., 2012). It remains unclear if marine animals can also release organic ligands in their fecal material.



Lastly, the the different oxidation states [Fe(II) or Fe(III)] influences the solubility of Fe. Fe(II) is considered to be the more bioavailable fraction because the thermodynamically stable Fe(III) redox species is less soluble (solubility of 0.07 nM in seawater of 4°C, pH 9 and salinity 36; Liu and Millero, 2002). In oxygen-rich waters, Fe(II) is rapidly oxidized into Fe(III) by oxygen and hydrogen peroxide. However, Fe(III) can be reduced to Fe(II) through photochemical reduction of colloidal Fe (Wells and Mayer, 1991; Rijkenberg et al., 2005) or reduction

of organically bound Fe(III) (Barbeau, 2006; Rijkenberg et al., 2006). The reoxidation of Fe(II) can occur quite rapidly in seawater ($t_{1/2}$ of 93.6 min at 4°C and pH 8; Croot and Laan, 2002). However, in the Southern Ocean, the cold temperatures (Millero et al., 1987), the presence of organic ligands (Gledhill and van den Berg, 1994; Boye et al., 2001; Maldonado et al., 2005; Barbeau, 2006; Hassler et al., 2012; Lannuzel et al., 2015), and generally low hydrogen peroxide concentrations (Sarhou et al., 1997) may slow the oxidation rates. At present, there is no information on the oxidation state of fecal Fe. The acidic digestion processes within the gut would favor the reduction of Fe(III) to Fe(II), however as the fecal material is expelled into an oxygenated environment, Fe(II) could return to an oxidized Fe(III). This is an area of further study.

Summary and Directions for Future Research

As discussed above, there is a suite of processes (e.g., grazing, predation, excretion/defecation, remineralization) involved in the transfer of Fe from herbivores to large carnivores, and the subsequent recycling and export of Fe (**Figure 1**). Pelagic herbivores appear to have two opposing effects on oceanic primary productivity. On the one hand, the high biomass of herbivores in marine ecosystems (Pakhomov et al., 2000; Atkinson et al., 2009), high grazing pressure on primary production (Perissinotto, 1997; Walsh et al., 2001; Smetacek et al., 2004; Sato et al., 2007), rapid gut passage time (Schnetzer and Steinberg, 2002; Tirelli, 2005; Schmidt and Atkinson, 2016), coupled with their fast sinking fecal pellets (Turner, 2015), suggests that herbivores play an important role in the export of Fe to below the mixed layer. On the other hand, the storage and release of Fe, and other essential nutrients, within the mixed layer (Tovar-Sanchez et al., 2007; Ortega-Retuerta et al., 2009) or through vertical migration (Schmidt et al., 2011) increases microbial productivity (Aristegui et al., 2014), and contributes substantially to Fe recycling (Maldonado et al., 2016). These different findings are likely due to the condition of the peritrophic membrane in zooplankton fecal pellets that acts as a protective mechanism, impeding the release of nutrients. Biological processes such as microbial degradation (Morata and Seuthe, 2014), and the loosening, fragmentation and ingestion of fecal pellets by other detritivorous animals (coprochaly, coprorhexy and coprophagy respectively) (Noji et al., 1991) can disrupt the membrane and release the incorporated nutrients into the water column.

The fate of any element ingested by herbivores is determined by the balance of predation behavior (i.e., surface feeding and defecating, vs. surface feeding but defecation at depth). As homeostatic regulation releases elements which are in excess to requirements, the transfer of Fe between successive trophic levels will differ from species to species based on their elemental requirements. Although we have focussed on Fe in this review, marine animals also recycle other nutrients through their diet and subsequent defecation such as labile dissolved organic carbon (DOC) which stimulates the DOC-limited heterotrophic bacterial community (Ruiz-Halpern et al., 2011; Aristegui et al.,

2014), macronutrients such as ammonium (Atkinson and Whitehouse, 2000; Tovar-Sanchez et al., 2009; Whitehouse et al., 2011; Lehette et al., 2012), and micronutrients such as Cd, Co, Cu, Zn, and Mn (Tovar-Sanchez et al., 2009; Ratnarajah et al., 2014), which might be important for marine primary production. In addition, some large predators defecate solely in the water column (e.g., whales), whilst others may defecate both in the water during periods of intensive feeding as well as on land and ice (e.g., seals, penguins etc.). The material defecated on land and ice could wash into the seawater during periods of sea ice melt and through strong winds that fractionate and disperse fecal material into the ocean.

A growing body of literature suggests that biological recycling by multi-cellular animals is clearly important to primary production, trophodynamics, and phenology. However, the main contributors remain to be distinguished and quantified. To date, multicellular animals have been largely implicated in downward nutrient transfer but there is increasing evidence that such animals can also play a role in retaining nutrients in the surface layer, returning nutrients to the surface waters and exporting nutrients to different areas of the ocean. Biological recycling influences the biological carbon pump, but there are some important questions that need to be answered to determine the degree to which it does.

The consistency of fecal material, and the length of time that the fecal particles remain in the mixed layer will influence its bioavailability for phytoplankton growth. Critical research will require: determining the fraction of dissolved to particulate Fe in fecal material, looking for the presence of organic ligands

released through grazing practices or defecation, examining the response of organic ligands in seawater to fecal derived Fe, and to the oxidation state of fecal material. It is also essential to determine the timeframe that fecal pellets or particles remain in the mixed layer before being exported, and what are the biological (e.g., remineralization, coprochaly, coprorhexy, and coprophagy) and physical (e.g., dissolution, fragmentation) processes involved in the degradation and release of fecal Fe during its transit. Answers to these questions will bring us closer to understanding if, and how, Fe is retained in the surface layer by marine animals. Ultimately, it will also be essential to quantify how much of the carbon taken in by animals is respired back into the atmosphere.

AUTHOR CONTRIBUTIONS

LR, SN, and AB: equally contributed to the analysis, interpretation, and drafting of the manuscript.

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Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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