Title: A “shallow bathtub ring” of local sedimentary iron input maintains the Palmer Deep biological hotspot on the West Antarctic Peninsula shelf.

Authors:
Robert M. Sherrell [1,6]*
Amber L. Annett [1,2]
Jessica N. Fitzsimmons [1,3]
Vincent J. Roccanova [1]
Michael P. Meredith [4]

[1] Department of Marine and Coastal Sciences, Rutgers University, 71 Dudley Road, New Brunswick, NJ, USA 08901
[3] Now at: Department of Oceanography, Texas A&M University, College Station, TX, USA, 77843

*corresponding author

ABSTRACT

Palmer Deep is one of several regional hotspots of biological productivity along the inner shelf of the western Antarctic Peninsula. Proximity of hotspots to shelf-crossing deep troughs has led to the “canyon hypothesis”, which proposes that circumpolar deep water flowing shoreward along the canyons is upwelled on the inner shelf, carrying nutrients including iron (Fe) to surface waters, maintaining phytoplankton blooms. We present here full-depth profiles of dissolved and particulate Fe and manganese (Mn) from eight stations around Palmer Deep, sampled in January and early February of 2015 and 2016, allowing the first detailed evaluation of Fe sources to the area’s euphotic zone.

We show that upwelling of deep water does not control Fe flux to the surface; instead, shallow sediment-sourced Fe inputs are transported horizontally from surrounding coastlines, creating strong vertical gradients of dissolved Fe within the upper 100m that supply this limiting nutrient to the local ecosystem. The supply of bioavailable Fe is therefore not significantly related to the canyon transport of deep water. Nearshore time-series samples reveal that local glacial meltwater appears to be an important Mn source but, surprisingly, is not a large direct Fe input to this biological hotspot.

Media Summary:

Situated in nearshore waters of the western Antarctic Peninsula, Palmer Deep is one of several regional hotspots of biological productivity. High phytoplankton growth suggests a
notably strong source of the limiting nutrient iron (Fe). Here, we provide the first measurements with which to test this hypothesis. We show that upwelling of deep water does not control Fe supply to the surface; instead, shallow sediments provide Fe inputs are transported horizontally from surrounding coastlines, at depths just below the surface, creating strong vertical gradients of dissolved Fe within the upper 100m, and supplying Fe to the local ecosystem.

KEYWORDS: iron, manganese, biogeochemistry, Antarctic, sediment, phytoplankton, nutrient

1. Introduction

The Southern Ocean south of the Polar Front is widely considered to be a High Nutrient Low Chlorophyll (HNLC) region, where phytoplankton biomass is limited in part by availability of the micronutrient Fe [1, 2]. Phytoplankton abundance increases with proximity to the Antarctic continent [3], leading to the presumption that Fe limitation is at least to some extent relieved by continental sources [4]. The Western Antarctic Peninsula (WAP) continental shelf region is characterized by high phytoplankton concentrations, as assessed by remote sensing, though with considerable spatial, seasonal, and interannual variability characterizing summertime blooms [5-9]. On the WAP shelf, phytoplankton biomass in summer (January) is higher generally on the inner shelf than on the outer shelf and seaward of the shelf break [5-9]. In particular, several inner shelf biological “hotspots” have been identified, where organisms at all trophic levels from phytoplankton [10] to penguins [11] are more abundant than in other coastal regions of the WAP. These hotspots, including Palmer Deep (PD), occur adjacent to the inner shelf termini of cross-shelf canyons, geological features resulting from ice scour during the last Glacial period. The hypothesis that the concentrated activity of higher organisms is driven by bottom-up mechanisms such as nutrient flux is supported by recent observations that phytoplankton biomass is indeed significantly higher in these regions [10], and that diatoms, critical prey and bottom-up controls on krill populations [12], compose an anomalously high fraction of the phytoplankton assemblage [10]. Recent work with autonomous gliders supports this view, and locates the high phytoplankton regions and coincident penguin foraging locales to the flanks of the canyon along sharp bathymetric gradients [11].

Only recently have data become available to support earlier hypotheses that the availability of Fe in the euphotic zone exerts a key control on the distribution of phytoplankton production over the WAP shelf [13-15]. These new findings were preceded by earlier work that focused on control of phytoplankton growth by mixed layer depth and light availability over the WAP shelf, with the implicit assumption that macro- and micronutrients were replete everywhere, but with no explicit mention of Fe [6]. A competing hypothesis argued that upwelling of Upper Circumpolar Deep Water (UCDW), which is variable in space and time on the WAP, determined which regions experienced high primary production and high fractions of diatoms, but did not speculate on a connection to Fe supply [16]. Garibotti et al. [8, 17] suspected that the seasonal progression of phytoplankton assemblages, expressed geographically in WAP surface waters, may result from Fe removal by early-blooming diatoms following sea ice retreat. A quarter century of data collected as part of the Palmer-LTER program [18] indicate that macronutrients are seldom exhausted in the WAP region [19]. This suggests that trace
elements and/or light control the distribution of primary producers on the shelf as a whole, as well as within the hotspots.

The “canyon hypothesis” posits that the locations of the biological hotspots [11] on the WAP are determined by the preferential upwelling of UCDW at the nearshore termini of the several canyons or troughs that traverse the shelf from the shelf break to the inner coastal regions. The implication is that the relatively high nutrient content of UCDW provides bottom-up support for high productivity in regions of upwelling, including the nearshore hotspots. Given the abundance of macronutrients in surface water throughout the WAP, including at PD, it is reasonable to assume that Fe is the critical nutrient supplied by the upwelled deep water. However, until the present work, no measurements of subsurface Fe concentrations in PD were available to test this idea.

Recently, the first description of the spatial distribution of potentially-limiting dissolved Fe (dFe) concentrations in surface waters on the WAP was presented for January of 2010, 2011 and 2012 [12]. It was found that, while in general the inner shelf regions are relatively rich in dFe, large regions of the mid- and outer-shelf have surface dFe concentrations low enough to potentially limit productivity of at least some members of the phytoplankton assemblage (<0.15 nmol kg⁻¹; similar to surface waters of the off-shelf polar Southern Ocean HNLC region [13]). A complementary study of springtime dFe distributions confirmed relatively high concentrations inshore, increasing with depth [14]. However, neither study included investigation of a nearshore hotspot with sufficient spatial resolution and sampling density to identify the specific mechanisms that could lead to high dFe flux to surface waters, or whether Fe delivery to hotspots is indeed related to UCDW upwelling.

Here we report an intensive study of dissolved and particulate distributions of Fe and Mn in the region of the PD hotspot, in the northern WAP adjacent to Palmer Research Station, in January of 2015 and 2016 (Fig. 1). This targeted investigation of hotspot micronutrient distribution refutes the canyon hypothesis that UCDW upwelling supplies the critical limiting nutrient. Instead, the results indicate that vertical mixing of laterally transported Fe derived from relatively shallow local sediments, at dFe concentrations exceeding those found in deep waters, provides the Fe flux that maintains the biological hotspot at PD.

2. Methods

a) Trace metal clean seawater collection:

Water column profile samples for this study were collected during the annual cruises of the RV Laurence M. Gould as part of the Palmer LTER program. The two 2015 cruise stations were collected on January 6 and 8, 2015 (15-24 and 15-48). During the 2016 cruise, three PD stations were sampled early in the cruise on January 11-12, 2016 (16-15, 16-24 and 16-31) and three were sampled late in the cruise on February 6-8, 2016 (16-394, 16-414 and 16-445; Fig. 1).

The methods employed for clean seawater collection were very similar to those used in the GEOTRACES program [20]. Seawater samples for iron analysis were collected using a trace metal clean (TMC) rosette composed of twelve Teflon-coated Niskin-X bottles mounted on a polyurethane-coated frame free of metal anodes. The rosette was deployed using a plastic-coated custom-designed winch and an aramid conducting cable through an anodized aluminum sheave. The Niskin-X bottles were stored and prepared in a metal-free clean room in the ship’s laboratory, constructed of plastic sheeting over an unpainted wooden frame and inflated
continuously with HEPA-filtered air to avoid metal contamination. Immediately before a cast,
each bottle was carried individually from the clean room and mounted on the rosette on deck.
Bottles were cocked and open for the minimum possible duration before deployment, to
minimize deck contamination. Bottles were closed on ascent while the package moved upward at
<10 m min⁻¹ to ensure that the seawater sample was collected as the rosette moved into clean
seawater. Filled Niskin bottles were returned to the clean room as soon as possible after
recovery.

Once racked in the clean room, each Niskin-X bottle was pressurized to ~0.5 atm using an air
pump and manifold fed by HEPA-filtered air and re-filtered just before entering each Niskin
bottle. An acid-cleaned piece of Bev-A-Line tubing was secured in the stopcock and rinsed with
sample seawater before an acid-cleaned Acropak-200 (0.2 μm) capsule filter was attached to the
line. After the filter was flushed with ~1 L of seawater, acid-cleaned LDPE bottles were filled
with filtered seawater following three ~10%-volume bottle rinses. Samples were acidified to
0.012 M HCl (pH ~2) using concentrated ultrapure acid (Optima grade, Fisher Scientific) and
stored until analysis.

Particulate samples were pressure-filtered at ~0.5 atm from 2-7 L of seawater using a Niskin-
mounted filter holders containing acid-washed 25mm Supor filters (0.45 μm), following the
methods of Planquette and Sherrill [21]. Excess seawater was removed by gentle suction, and
filters were then frozen in acid-cleaned polystyrene Petrislides until analysis. All equipment was
acid washed prior to use.

Surface water was collected at LTER Station E (6.5 km NE of the head of PD; Figure 1),
using an acid-cleaned all-polypropylene syringe and 0.45 μm pore size Supor syringe filter.
Sampling was completed while leaning over the side of a slowly-moving inflatable Zodiac boat,
as detailed in Carvalho et al. [22]. Samples were collected in duplicate during 11 one-day
expeditions between January 5 and March 9, 2015. The mean of the duplicates is reported if they
agree within ±15% (difference about the mean), otherwise the lower of the two values is
reported.

b) Dissolved and particulate trace metal analysis:

Stored acidified filtered seawater samples were analyzed for Fe and Mn (as well as Zn, Cu,
Ni, Cd, and Pb; to be reported elsewhere) using an offline commercial version of the isotope
dilution-inductively coupled plasma mass spectrometry (ICP-MS) method of Lagerström, Field
[23], using procedures similar to those described in detail in Annett et al. [13]. In short, 10 mL
aliquots of seawater samples were automatically extracted using the commercially available
SeaFAST pico system (Elemental Scientific, Inc.) after online buffering to pH ~6.5 using
ammonium acetate and a 25-fold pre-concentration into 10% v/v ultrapure nitric acid (Optima
grade, Fisher Scientific). The standardization of Fe employed the method of isotope dilution,
while Mn was standardized using external matrix-matched standards that were extracted and pre-
concentrated identically to samples. Extracts were analyzed using an Element 1 sector-field ICP-
MS (Finnigan MAT). Accuracy was assessed by repeated measurements of SAFe surface (SAFe
S) and deep (SAFe D2) Pacific Ocean reference seawater samples. Our measurements of SAFe S
gave Fe=0.102±0.021 (n=29 over a 2-month period; consensus 0.093±0.008) and Mn=1.00±0.05
(n=34 over a 2-month period; consensus 0.79±0.06). Our measurements of SAFe D gave
Fe=0.968±0.066 (n=39 over 1 year; consensus 0.933±0.023) and Mn=0.48±0.02 (n=37 over 1
year; consensus 0.35±0.05). Consensus values are from the most recent May 2013 compilation
Precision, determined by replicated analysis of two different in-house large-volume reference seawater samples within each analytical session, was typically ±3% or better.

In a trace-metal clean laminar flow hood, particulate filters were cut in half to provide samples for both total particulate digestion and leachable metal content, using a new surgical stainless steel razor blade for each profile. Filter halves were digested for total particulate metals using an HNO$_3$/HF solution and ICP-MS analysis for a large suite of elements, following the method of Planquette and Sherrell [21]. Filter halves for leachable metals (LpFe and LpMn) were heated (~90°C) for 10 minutes in 25% (v/v) ultrapure acetic acid solution (Optima grade, Fisher Scientific) with a small addition of hydroxyl amine reducing agent [24], left to cool slowly for 2 hours, and centrifuged. The supernatant was removed with an acid-rinsed pipette to a clean Teflon PFA vial, 100 uL concentrated HNO$_3$ was added with 30 ng of Cs as a yield tracer, and the sample dried down on a Teflon-coated hotplate in a HEPA filtered-air fume hood. Another 100 uL concentrated HNO$_3$ (Optima grade, Fisher Scientific) was added and the sample was dried down again to digest and drive off remaining leaching solution organic compounds. The residues were re-dissolved in a 5% (v/v) HNO$_3$ solution (Optima grade, Fisher Scientific) by heating at 95°C for 2 hours with vial caps tightened. Samples were then analyzed by ICP-MS as for total particulate digests.

c) Seawater oxygen isotope ratio analysis:

Samples were collected from the ship’s CTD/rosette (deployed at the same stations and typically within 2 hours of the TMC CTD deployment) during the annual cruises of the RV Laurence M. Gould as part of the Palmer LTER program. Samples were also collected from the surface and/or 10m at Station E during quasi-weekly water column profiling, as described above. Samples were stored in 50mL glass bottles, which were sealed with stoppers and aluminum crimps, and subsequently transported to the Natural Environment Research Council (NERC) Isotope Geosciences Laboratory at the British Geological Survey, UK, for determination of the ratio of stable oxygen isotopes in seawater ($\delta^{18}O$, being standardized values relative to Vienna Standard Mean Ocean Water, VSMOW). A VG Isoprep 18 and SIRA 10 mass spectrometer was used for analysis, with duplicate analyses revealing a precision better than 0.02‰. Paired $\delta^{18}O$ and salinity data were used in a simple 3-endmember mass balance to quantify separately the contribution to the freshwater budget from sea ice melt (%SIM) and that from meteoric water (%MET; the sum of glacial discharge and precipitation into the ocean). This endmember balance method was developed originally by Östlund and Hut [25], and has been implemented at the WAP for both coastal and shelf-wide freshwater studies (e.g. Meredith et al. [26]). The values of the endmembers used here (i.e. the values of the “pure” forms of oceanic water, sea ice melt and meteoric water prior to these endmembers mixing to form the waters sampled) were, respectively, salinity = 34.73, 7, 0 and $\delta^{18}O$ = 0.1, 2.1, -16; typical errors in the derived freshwater contributions are better than 1%. Full details are provided in Meredith et al. [26].

3. Results

a) Hydrographic variables

The potential temperature and salinity profiles are within the range of those observed previously at this inner shelf region [22]. The temperature is generally variable in surface waters, depending on local variations in the recent history of solar warming, heat and water flux, sea ice
melting, and mixing (Fig. 2). Below this lies a Winter Water (WW) layer with potential

temperature about -1.2°C for most stations. Station 15-48, furthest from shore (Fig. 1), had the

thickest and deepest WW within the interval 50-100 m (unfortunately because of competing

sampling demands, no metals samples were taken in this depth interval). Late season 2016

profiles on the shallow flanks at the head of the canyon (16-414 and 16-445) had the warmest

upper water column profiles overall, and the strong temperature minimum evident at 20-50 m at

the nearby earlier stations 16-24 and 16-31 was apparently eroded by mixing with warmer water

above and below, even to a greater degree than observed with glider data at the flank stations

collected just 3-4 days prior (compare Fig. 2 to Fig. 6 of Carvalho et al. [22]). The regionally

modified UCDW endmember is generally found at depths >400 m, and is characterized by

potential temperature ~1.4°C and salinity ~34.7.

b) Dissolved Fe

Dissolved Fe concentration profiles at the eight PD CTD stations were relatively similar

except at the most coastal station, located south of PD (16-394), and displayed modest but

significant differences reflecting geographical position and temporal variation (Fig. 3a,e; Table

S1). The dFe was moderately low in the upper 20m (most values 0.2-0.5 nmol kg\(^{-1}\) up to 0.8

nmol kg\(^{-1}\) at two stations; Fig. 3a,e) and increased approximately linearly to maxima as high as

3.5 nmol kg\(^{-1}\) found at depths ranging from 75-200m, then decreased to 1.8-2.5 nmol kg\(^{-1}\) near

400 m. The two 2015 stations near the middle of the canyon (15-24 and 15-48) showed slight

increases in dFe from 400 m to the bottom (1200-1300 m), with maximum concentrations as

high as 2.6 nmol kg\(^{-1}\) at 10 m off the bottom. Station 16-15 was unique in showing the deepest

maximum (200 m), anomalously high concentrations from 400-700m, and lower concentrations

below 700 m than the 2015 deep stations, with no increase to the sediments. Overall most

two samples in the core of the UCDW (>400 m) had dFe concentrations of 2.0-2.5 nmol kg\(^{-1}\).

Among the stations in the NE sector of the sampling region in the vicinity of the head of

the canyon and closest to Palmer Station (Fig. 1), the stations over the northern flank, 16-24 and

16-414, had relatively deep dFe maxima between 100 m and 200 m. These maxima also had

higher concentrations than those over the southern flank (16-31 and 16-445) which occurred

shallower, at 75-100m. In addition, the canyon head stations that were occupied 27 days later in

the cruise (16-414 and 16-445) had lower dFe overall through the upper 200 m than the nearby

but earlier-occupied stations (16-24 and 16-31, respectively), representing apparent temporal

variability in dFe concentrations in this region, although a role for short spatial gradients cannot

be ruled out.

Notably, the southern coastal Station 16-394 differed strongly in dFe distribution from all

other stations, with high concentrations of 1.1 nmol kg\(^{-1}\) in surface waters (5 m), increasing

strongly to a local maximum of 7.3 nmol kg\(^{-1}\) at 50 m (Fig. 4). This maximum was followed by a

slight decrease to 6.9 nmol kg\(^{-1}\) at 65 m, and thereafter a linear increase to the very high value of

12.4 nmol kg\(^{-1}\) near the bottom at 289 m. These results suggest a strong nearshore Fe source

throughout the upper 300 m in this PD region south of the canyon.

c) Dissolved Mn

While dFe which varied spatially by <3-fold in the surface waters, dMn was much more

variable, exhibiting a 10-fold range in surface waters (Fig. 3c,g; Table S1). Surface maxima were

observed only at Stations 15-24 and 15-48, where surface dMn was 4.1 and 2.6 nmol kg\(^{-1}\),

respectively. The 2015 surface value of 4.1 nmol kg\(^{-1}\) over the middle of the canyon (LTER grid
station 600.040; Fig. 1) was the highest surface water dMn measured in the region, despite the
distance from coastal sources. The surface dMn variations at the other stations (0.6-2.9 nmol kg\(^{-1}\)
at 5-10 m depth) reflected varying degrees of local surface minima. All stations except three (15-24,
15-48 and 16-394) showed similar local subsurface dMn maxima of 3.0-4.2 nmol kg\(^{-1}\) at
similar depths (50-65 m) and isopycnals, shallower and stronger than the dFe maxima. Below
these maxima, dMn decreased rapidly and similarly for most profiles to values near 1.0 nmol kg\(^{-1}\)
at 400 m, though 15-24 was a higher outlier. Stations 15-24 and 15-48 showed nearly vertical
dMn profiles at ~1.0 nmol kg\(^{-1}\) from 400 m to the bottom, while dMn at 16-15 was also nearly
homogenous in this depth interval, but was significantly lower at ~0.8 nmol kg\(^{-1}\). Coastal station
16-394 was anomalous in having a very strong subsurface maximum of 8.8 nmol kg\(^{-1}\) at 35 m,
coincident with particulate Fe and Mn peaks (Fig. 4). Below this maximum, dMn decreased very
rapidly to 5.3 nmol kg\(^{-1}\) at 50 m, and more slowly below that to a minimum of 3.3 nmol kg\(^{-1}\) near
the bottom, remaining at roughly twice the concentrations found in the canyon stations (Fig. 3c).

d) Particulate Fe

Much higher concentrations of Fe were observed in suspended particulate form than in
dissolved form, over the entire water column at all stations. Total suspended particulate Fe (total
particulate Fe; TpFe) showed very strong variability with depth and between stations (Fig. 3b,f;
Table S1). In general, TpFe was at minimum concentrations in surface waters, though the
minimum varied from 1.2 to 12.4 nmol kg\(^{-1}\) at the open water sites. A surface local minimum as
also observed at coastal Station 16-394, but it was much higher at 127 nmol kg\(^{-1}\). Subsurface
local maxima in TpFe, of strongly varying intensity, occur within the interval 75-200 m (except
16-394, which had a shallower maximum at 35m). Concentrations of TpFe at the 75-200 m
subsurface maximum varied from ~20 nmol kg\(^{-1}\) at 15-48 and 16-24, to a very sharp peak of 155
nmol kg\(^{-1}\) at 78 m at 16-445, to a volumetrically huge peak centered at 35 m at the south coastal
station 16-394, with maximum TpFe at the highest value found in this study (230 nmol kg\(^{-1}\)).
This southern coastal station had the highest Fe concentrations at all depths (Figs. 3, 4), even
though concentrations decreased from the 35 m maximum to a minimum of 100 nmol kg\(^{-1}\) near
the bottom. For comparison, the highest TpFe found in the Amundsen Sea embayment, ~120
nmol kg\(^{-1}\), was observed in near-surface waters adjacent to the Crossen Ice Shelf [27]. At the
depth canyon stations of PD, TpFe increased roughly 2-fold from 500 m to the bottom, to
maximal values for these stations of 50-65 nmol kg\(^{-1}\) at 1210-1320 m. These deep and thick
nepheloid layer signals were either not observed or were very subtle in the shallower stations to
northeast and south, with bottom depths at ≤500 m.

e) Particulate Mn

Suspended particulate Mn (total particulate Mn; TpMn) showed strong spatial variability
in the upper 50 m, with profiles from 50-400 m that were similar in shape to TpFe, but much
lower in concentration (Fig. 3d,h; Table S1). Opposite to the Fe speciation, dMn exceeded TpMn
at most near-surface locations, and TpMn was at a minimum in near-surface waters of most
stations. The canyon head stations 16-414 and 16-445 and also the coastal 16-394 were
exceptions in having a local TpMn maxima at or near the surface (Figs. 3d, 4). Subsurface
maximum TpMn concentrations occurred in the 75-150 m interval, generally corresponding in
depth to the TpFe maxima at the same stations, with maximum values <4 nmol kg\(^{-1}\) (except for
coastal station 16-394; Fig 4). For deep stations near the center of PD, a second and larger
maximum occurred at or near the bottom, with an increasing gradient to this maximum starting at
500 m, though with a lesser relative gradient to the bottom than for TpFe. As for TpFe, these near-bottom increases in TpMn were absent (or nearly so) for canyon slope stations 16-24 and 16-31.

f) Comparison of dissolved and particulate pools

The relative profiles of dissolved and particulate Fe and Mn, including the weak acid leachable fraction (LpFe, LpMn), are displayed for three characteristic stations in Fig. 5. The labile fraction of Fe (LpFe) generally accounts for less than half the total particulate Fe (TpFe) but its relative contribution increases in offshore near-surface waters as in Station 15-24. In contrast, LpMn accounts for more than half of TpMn in the upper 50-100m and nearly 100% in the upper 20m of Stations 16-414 and 16-445 (Fig. 5; Table S1). However, the contribution of LpMn decreases to less than half of TpMn in the deeper waters of all stations at which labile particulate metals were determined (Fig. 5; Table S1).

g) Glacial meltwater and precipitation

The distribution of oxygen isotope values in surface waters at all stations (Fig. 2). Meteoric water contributed 3-4% volumetrically in the upper 20 m at all stations, when calculated relative to the CDW endmember. Despite its location in the center of PD, well offshore, Station 15-24 had high %MET in surface water and the highest meteoric fraction mixed down to 200 m, with ~1% at 200 m. Occupied one year later at the same location, Station 16-15 had significantly lower %MET throughout the upper 200m. In contrast, at the coastal station 16-394 the %MET decreased rapidly from a surface maximum just over 4% to <0.5% at 50 m, with a slight decrease thereafter to the bottom. The other profiles fell between these bounds, although the late-cruise 2016 stations near the canyon mouth (16-414 and 16-445) showed essentially no meteoric component below 100 m, within the errors of the calculation.

h) Sea ice melt

The profiles of %SIM show values in the range -1 to +1% over most of the water column sampled (Fig. 2). Negative values here denote waters that were subject to net sea ice formation prior to being sampled, though the low values observed are generally not significantly different from zero. The exception to this pattern is the upper 20-30 m, over which there is often a modest increase towards the surface, with some values exceeding +2%, indicative of variable summer-season sea ice melt at the surface. There does not appear to be a consistent relationship between %SIM and trace metal distributions.

i) Station E surface dissolved metals

In the surface waters of Station E, roughly 3 km south of Palmer Station (Fig. 1), dFe varied widely from 0.6-6.9 nmol kg\(^{-1}\) (previously reported in [22]), and dMn from 0.7-3.8 nmol kg\(^{-1}\) (Fig. 6). The temporal variations in dFe and dMn displayed an anti-correlation overall; dMn was lowest when dFe was highest, and vice versa. The CTD profiles taken at each sampling event allowed mixed layer depth (MLD) to be calculated, using the methods of Carvalho et al. [22]. The dFe concentrations were low through much of January, and MLD shallow. When MLD deepened to 39 m at the onset of a windy February [22] dFe increased sharply to its maximal value of 6.9 nmol kg\(^{-1}\), while dMn fell to its minimum value of 0.76 nmol kg\(^{-1}\). The MLD deepened to 76 m on the next sampling occasion, and dFe fell to 3.8 nmol kg\(^{-1}\). Through the rest
of the sampling period, dFe continued to fall and dMn to rise slightly, until the last sampling date when MLD shoaled and dFe dropped to near the January levels. The %MET in these surface waters (sampled at 0 m or 10 m) remained between 3% and 4% over the entire sampling period, with a broad subtle maximum centered in late January.

DISCUSSION

4. A shallow sub-surface dissolved Fe maximum.

The PD region has been described as one of three regional WAP hotspots of biological productivity at all trophic levels, with maximum phytoplankton productivity typically in January [10]. The high productivity has been described as resulting from upwelling, driven by winds and the regional canyon bathymetry [11] with the implication that nutrient supply from below makes this region especially productive, encouraging krill growth [28], supporting seabirds and mammals [29] and maintaining a local penguin colony near Palmer Station [30]. At the same time, because macronutrients are rarely drawn down to limiting concentrations in this region and on the WAP shelf overall, it was inferred that the supply of micronutrients (e.g. Fe; [2]) from upwelled UCDW allowed the PD euphotic zone to be more productive than surrounding inner shelf regions (though see an alternative view, [31]). From previous studies of trace metal distributions in the off-shelf deep Southern Ocean, it was realized that dFe was more concentrated in UCDW than in surface waters of the Southern Ocean overall [14, 32], and incursions of UCDW along cross-shelf canyons were thought to supply the hotspots, including PD, with Fe sourced from deeper off-shelf waters, brought to the PD euphotic zone by upwelling following the long transit to the inner shelf [33]. However, none of these earlier studies had access to water column Fe data with which to test this hypothesis.

The data presented here show that modified UCDW (potential temperature ~ 1.4°C), found in the deeper regions of PD (>400 m at most stations), carries about 2.0 nmol kg\(^{-1}\) dFe, indicating that it is certainly enriched during its transit across the shelf, relative to the off-shelf open ACC UCDW endmember (dFe ~0.4 nmol kg\(^{-1}\) [14]). However, our results reveal a shallower dFe maximum of ~2-4 nmol kg\(^{-1}\), centered at 75-200m, falling in the upper part of the mixing zone between UCDW and WW, and much shallower than the core of the UCDW. The proximity of this relatively shallow dFe maximum to the euphotic zone indicates that this feature is the primary driver of the strong upper water column gradient in dFe that supplies the PD euphotic zone with the limiting micronutrient through vertical diffusion and wind-driven mixing events. The surface dFe concentrations of 0.2-0.8 nmol kg\(^{-1}\) are substantially higher than those found in surface waters of the outer shelf or seaward of the shelf break in the open Southern Ocean [13]. The details of Fe availability and biological response are beyond the scope of this paper, but the relatively high surface dFe concentrations are consistent with the PD hotspot phytoplankton being Fe-replete overall in January, allowing variations in productivity to be controlled largely by light availability and MLD (F. Carvalho pers. comm.). Overall, we see very little resemblance between dFe or TpFe concentrations and endmember water masses as defined by temperature/salinity characteristics (Fig. 2, inset), consistent with our interpretation that Fe distributions that are controlled by local sources and sinks rather than by mixing of water masses with well-defined Fe concentrations.
5. A dominant sedimentary Fe source is indicated by suspended particle distributions.

The source of the upper water column dFe maxima is informed by the distribution and composition of suspended particles. At every station measured in this study, TpFe shows a sub-surface maximum at 75-200m, the magnitude of which decreases in general with distance from shore (Fig. 3b,f). The comparison of leachable particulate Fe (LpFe) to total particulate Fe (TpFe) suggests that suspended Fe exists mostly within refractory terrigenous particles (LpFe ~12-36% of TpFe; Fig. 5, Table S1), an assertion reinforced by total particulate Fe/Al ratios that are very close to the crustal mean value (data not shown). While the depth of the peak varies by station, the range of seawater densities at which the TpFe maxima appear is fairly narrow, at $\sigma_t = 27.44-27.71$. In particular, stations sampled close to each other in time tend to have TpFe peaks falling at very similar densities even if they are at different depths; for example, the shallow sharp peak at 16-445 (southern flank; Fig. 1) occurs on almost exactly the same density surface ($\sigma_t = 27.61$ at 78m) as the broader deeper peak at 16-414 (northern flank; $\sigma_t = 27.63$ at 100m).

The TpFe peaks increased sharply from the PD center and slope to the shallower flanks near the mouth of the canyon (16-24 vs. 16-414 and 16-31 vs. 16-445 in Fig. 3b,f) and even more so to the very coastal station 16-394 (Fig. 4). While there is a possibility of substantial temporal variation over the period of the cruise, especially in the upper water column and in association with the early February wind mixing event, the characteristics described here overall suggest strongly that the TpFe peaks resulted from lateral advection of fine resuspended sediment occurring along the coast or near proximal islands, at 50m or shallower. The resulting suspended particles then roughly followed isopycnals during horizontal eddy diffusion and advection, the peaks broadening and attenuating under the influence of vertical mixing and particle sinking during transport to the sampling sites. Consistent with a coastal source and lateral dispersal, we note that the lowest TpFe concentrations in the upper 300m are found at the most distal Station 15-48 (Fig. 3f).

At all stations, the dFe maximum occurs at or just below the upper water column TpFe maximum. The depth relationships are illustrated by three representative stations where TpFe peaks range in magnitude and occur at different depths (Fig. 5). In each case, the dFe peak was vertically broader than the corresponding TpFe peak, maintaining high values for tens of meters below the peak, whereas the TpFe decreased with depth below the maximum. For example, at PD Station 15-24 (Fig. 5a), the TpFe maximum of 34 nmol kg$^{-1}$ occurred at 75m, and peaks of 10 nmol kg$^{-1}$ LpFe and 2.8 nmol kg$^{-1}$ dFe were centered one sampling depth deeper (100m). As well, down to 500m, the dFe and TpFe profile shapes follow each other fairly closely, at a dFe:TpFe molar ratio of ~1:10. This suggests a strong relationship between TpFe and dFe, and that both derive from a common sedimentary source. At Stations 16-414 and 16-445, the TpFe peaks are much larger than at 15-24 but dFe remains in the 2-3 nmol kg$^{-1}$ range. A reasonable assumption is that the concentration of dFe is controlled by the concentration of soluble organic ligands and by the presence of <0.2 $\mu$m colloidal Fe particles. It is also reasonable to assume that dFe has a much longer residence time than TpFe, and thus integrates any temporal variations in the depths at which sedimentary sources are injected into the water column at some distance from the measured stations. The main source of Fe to the upper water column can thus be viewed as a “shallow bathtub ring” of coastal sediment inputs surrounding PD to the north, east and south, that are mixed and advected into the central canyon region of this biological hotspot. The dominance of a sedimentary source is similar to recent findings showing efficient vertical mixing.
of a sedimentary Fe sources to feed phytoplankton blooms over a shallow bank on the outer Ross Sea shelf [34, 35].

The mechanistic relationship between dFe and sediment resuspension is difficult to determine from the available data. The dFe may be sourced from shallow porewaters with high dFe concentrations that are “mined” during resuspension events and released into the water column. These porewaters may be highly enriched in soluble Fe(II) through shallow anaerobic respiration [32, 36], or may be enriched in Fe(III) stabilized by high concentrations of dissolved strong organic ligands resulting from the early diagenesis of organic matter at the sediment surface. A second potential source mechanism is that surface sediment LpFe (likely some form of Fe(III)) is resuspended along with refractory TpFe, and upon exposure to excess Fe ligands in the water column or to sufficient energy to physically disaggregate a subset of these particles into the colloidal size fraction (<0.2 μm), releases Fe(III) the dFe pool.

It is informative to note the unique dFe profile shape at Station 16-394, which has a local maximum just below the TpFe maximum, as at other stations, but then displays a linear increase to very high near-bottom concentrations of >12 nmol kg⁻¹ (Fig. 4). This suggests that the nearby deeper coastal sediments are a very strong source of dFe that does not scale with resuspension intensity. This same profile type is common in Ryder Bay, another very coastal site that does not impinge directly on a biological hotspot [37], but at that site dMn increases in parallel to dFe, while at 16-394 dMn decreases to the bottom (Fig. 4). Thus, different metal source processes are at play at Ryder Bay and 16-394; more generally, the mechanisms governing the Fe:Mn ratio of dissolved inputs from sediments are not well understood [36]. We speculate that both dFe and stabilizing dissolved ligands are released from coastal sediments at this station and likely from shallower sediments shoreward of the station. Station 16-394 is unique in displaying a nearly vertical density distribution from 100m to the bottom (θ₀ = 27.62-27.68), within the range of densities at which the dFe peak is seen offshore, and is therefore a possible source for the offshore dFe maxima. The divergence of the pFe and TpFe profiles below ~75m suggests that dFe sources need not be associated strictly with sediment resuspension. The details of processes occurring proximal to the coastal Fe sources deserve further study.

6. Glacial meltwater is a minor source of Fe to the Palmer Deep hotspot euphotic zone.

At most stations, dMn exhibited upper water column maxima that were considerably shallower than the dFe peaks (Figs. 3-5). This difference can be interpreted as a result of the relative importance of glacial meltwater as a source of dFe vs. dMn to the upper water column in the PD region. While it is tempting to suggest that these dMn peaks also derive from shallow sediments, they are often shallower by one or two sampling depths than the TpMn peaks (Fig. 3 c,d,g,h) that in turn tend to match the depths of the TpFe peaks, suggesting a combined TpMn and TpFe source from sediment resuspension. As well, the dMn is quite variable in surface waters, and 4 of the 8 profiles have local or absolute maxima at or near the surface (15-24, 15-48, 16-15 and 16-394; Figs. 3, 4). We hypothesize that the distribution of dMn in the upper 100m results primarily from a meteoric water source (assumed dominated locally by glacial meltwater; [38]), which we have shown is maximal at the surface (Fig. 2c,g), followed by variable drawdown of dMn by biological and scavenging processes occurring in the upper 50m, inducing a subsurface dMn peak as a byproduct of dMn removal in the uppermost water column, rather than as a reflection of a subsurface lateral source of dMn at that depth. By this reasoning, the stations with dMn maxima at the surface are the least altered from their near-shore source,
presumably a result of minimal biological removal relative to other stations (as for 15-24 and 15-48), or by virtue of being very close to a meltwater source (as for 16-394). The Station 16-15 profile suggests that removal of a meltwater source had only affected the shallowest sampled depth; otherwise the profile in the upper 75m is quite similar to the profile taken a year earlier in the same location (15-24; Fig. 3g). Some of the profiles show TpMn increases to surface or near-surface maxima within the upper 50m (16-24,16-414 and 16-445, Fig. 3d; 16-394, Fig. 4), that are not accompanied by TpFe peaks. In these near-surface waters, LpFe increases to the surface and becomes the major fraction of TpFe (Fig. 5). We speculate that the near-surface LpMn (and TpMn) thus represents the complementary manifestation of the near-surface conversion of meltwater-sourced dMn into the labile particulate phase, probably by a combination of phytoplankton uptake and bacterial oxidation [39]. Homogeneous oxidation of Mn(II) by O\(_2\) takes many years (~10\(^7\) times slower than Fe(II) oxidation; [40]) but a role for heterogeneous inorganic oxidation in the catalyzing presence of MnO\(_2\) particles cannot be ruled out in this environment [41, 42].

Importantly, dFe shows none of this sort of behavior; it is uniformly low in surface waters at all stations. This contrast in the behavior of dMn and dFe is consistent with the combined effects of a high dissolved Mn:Fe ratio in glacial meltwater and relatively greater dFe removal after input and during lateral transport within the surface layer. Indeed, measurements of glacial meltwater streams from Marr Glacier, adjacent to Palmer Station (Fig. 1) show strong variability but average dMn ~1600 nmol kg\(^{-1}\) (possibly reflecting anoxia in the subglacial hydrologic system) and a mean dMn:dFe molar ratio of ~7 (full meltwater data to be presented elsewhere). The single sample reported in Annett et al. [13] turns out to be atypical in having anomalously low dMn and a dMn:dFe ratio <1. We conclude that glacial meltwater has a large effect on dMn but a small effect on dFe distributions in the broader PD region.

This conclusion is at odds with the recent description of surface water dFe and dMn spanning three summers over the whole WAP shelf region [13], which showed evidence of a broad, imperfect and variable, but significant, correlation between dFe and %MET for surface waters of the entire WAP shelf region, but no such correlation for dMn. One possible reconciliation of these observations is that on the larger regional scale, shallow vertical mixing and variable biologically-mediated removal of both metals combines the \(^{8}\)\(^{18}\)O and dMn signal of meltwater with the initially deeper dFe signal to result in inter-relationships among these quantities that are highly variable and when measured in offshore waters may not reveal clearly the controlling processes at and near the coastal sites of input. It is also possible that glacial meltwater composition near Palmer Station is not typical of inputs to the wider WAP. Further measurements of various glacial meltwater streams and proximal coastal waters will be required to better understand the effects of glacial melt on the WAP as a whole. Nonetheless, the data presented here strongly suggest that for the PD region, glacial meltwater inputs have little effect on dFe distributions.

7. Further clues from time-series sampling of coastal surface water.

The fundamental findings of this work, a strong meltwater source of dMn and a subsurface sedimentary source for dFe for the PD region, are supported by the early 2015 time-series sampling of dissolved metals in surface water at Sta. E, located ~3km south of Palmer Station in ~100m of water. Surface water dFe through much of January varies about a mean of about 1 nmol kg\(^{-1}\)(Fig. 6) only slightly higher than the highest surface water seen at the more
offshore stations (Fig. 3a) and very similar to surface waters at coastal Station 16-394. Over the same period, dMn is relatively high, averaging ~3 nmol kg\(^{-1}\). However, an increase in mixed layer depth from 13 m to 39 m on the 9 February 2015 sampling was accompanied by a strong increase in dFe to near 7 nmol kg\(^{-1}\), similar to the value of the peak dFe at 50m depth at Station 16-394 (Fig. 4). At the same time, dMn fell to 0.8 nmol kg\(^{-1}\). Upon subsequent deepening of the MLD to 76 m, dFe fell to 3.8 nmol kg\(^{-1}\), while dMn increased slightly. Over late February into March, surface dFe continued to decrease while dMn rose slowly. Overall for the time-series dFe and dMn are negatively correlated.

We interpret this temporal sequence to indicate a surface enrichment of dMn, but little dFe, from nearby meltwater sources when MLD was shallow. When a wind event mixed the water column to several tens of meters depth, we suspect that the sharp increase in surface dFe resulted from upward mixing of a strong pre-existing gradient to high dFe in the subsurface, while at the same time the pre-mixing-event surface enrichment of dMn was diluted with lower-dMn water from below, assuming dMn was maximal at the surface before the mixing event (profile similar to 15-24 in shape; Fig. 3g). Over the subsequent sampling period, deep mixing continued, and dFe was preferentially removed by continued biological uptake and scavenging, while dMn increased somewhat, likely a result of continued surface meltwater inputs. It may seem curious that the fraction of meteoric water varies little (between 3 and 4%) over this sampling period, with no anomaly evident during the mixing event. While only surface water data are available, we speculate that this is because %MET varies comparatively little with depth, a result of accumulation and continuation of meteoric water inputs as reflected by this conservative tracer. The surface time-series, though limited in scope, thus provides a window into nearshore vertical Fe and Mn distribution. While it appears that high dMn can be traced to a meltwater source if MLD remains shallow, this is not true for dFe. Instead, near-shore sedimentary sources provided high dFe within the upper 50m and overwhelmed any meltwater Fe source to this region, though not necessarily over the entire WAP shelf.

8. Conclusion

These new trace metal data strongly suggest that sedimentary inputs in nearshore regions surrounding PD – the “shallow bathtub ring” – are the primary source for bioavailable Fe to the upper water column and thence to phytoplankton in the euphotic zone of the hotspot. The idea that upwelling of deep modified UCDW provides the key micronutrient for this biological hotspot is thus obviated and likely irrelevant, as the vertical dFe gradient to the surface is governed by the sediment-sourced sub-surface maximum at 75-200m, not by the lower Fe content local deep water found at >400 m. Interestingly, this implies that at least some marine-terminating glaciers in this region may have grounding lines that are quite shallow, as resuspension would require sediment that is not ice covered. Alternatively, unglaciated islands or regions of the mainland may be preferential sedimentary Fe sources, and glacial meltwater may also transport fine sediment into coastal waters; clearly, better knowledge of regional circulation [31] and the depths of glacial termini grounding lines within the upper 200 m near PD [43, 44] would be helpful in identifying specific sedimentary Fe source regions.

These findings suggest that a critical characteristic of the subsurface Fe source is that it is below the zone of rapid biologically-driven removal within the surface mixed layer, likely enhancing the broad dispersal and relatively continuous nature of the Fe input. Also, wind-driven
vertical mixing events may be crucial to provide sufficient Fe flux to the phytoplankton assemblage to maintain the uniquely high productivity of the PD hotspot [10]. Therefore, the existence of the hotspot does not result from upwelling of deep water, driven by canyon bathymetry, but instead seems dependent on bottom shear stress in shallow sedimentary regions surrounding the PD. On the basis of the PD example, we propose that canyons per se may be less relevant to hotspot location than previously thought, although the bathymetry of their flanks may encourage the necessary upward mixing of the strong local subsurface Fe supply. Further, the continuing retreat of marine-terminating glaciers on the peninsula [43] may enhance Fe delivery to this and possibly other coastal regions, not via the commonly assumed mechanism of increasing meltwater flux, but rather by exposing additional regions of shallow sediments, which could then serve as important new Fe sources to the upper water column of WAP inner shelf.

COMPETING INTERESTS: We have no competing interests.

AUTHOR CONTRIBUTIONS
RS conceived the study, supervised the 2015 field work and all of the data production, and drafted the manuscript. AA collected field samples in 2016 and analyzed the particulate samples. JF collected field samples in 2015 and supervised the field effort in 2016. VR analyzed the dissolved trace element samples. MM provided the oxygen isotope data, conducted the mass balance calculations, and interpreted the results. All authors critically edited the manuscript and gave final approval for publication.

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DATA ACCESSIBILITY
Data are made available in the attached Excel file “Sherrell Table S1-Dataset+legend”.

ELECTRONIC SUPPLEMENTARY MATERIAL
Excel file “Sherrell Table S1-Dataset+legend”.

REFERENCES


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Figure 1. Map of Palmer Deep study region off the Antarctic Peninsula. Stations designated YY-# where YY is cruise year and # is event number, were sampled from surface to bottom in 2015 (closed squares and blue triangle) and 2016 (closed circles). The Palmer LTER grid station 600.040 in the deepest part of the canyon was occupied in each year (red circle). Station E (blue triangle) was sampled over a time-series in January-March, 2015, in surface waters only.
Figure 2. Hydrographic data from the eight stations, with shallower stations in the top panels and deeper canyon stations in bottom panels. Plotted left to right are (a,e) potential temperature, (b,f) salinity, (c,g) % meteoric water contribution and (d, h) % sea ice melt. A T-S plot for these stations is shown as inset on lower salinity graph. Station color designations are consistent with Figure 3.
Figure 3. Vertical distribution of (a,e) dissolved Fe (dFe), (b,f) total particulate Fe (TpFe), (c,g) dissolved Mn (dMn), and (d,h) total particulate Mn (TpMn). Bottom sample collected at ~10m off bottom in each profile. Station 16-394 (solid black circles) runs off scale, but is shown in full detail in Figure 4. Open circles indicate canyon head stations sampled on the north and south flanks late in the research cruise (February 7-8), 27 days after the nearby stations (Fig. 1) indicated by filled circles of the same color.
Figure 4. Vertical profiles of dissolved (open symbols) and particulate (closed symbols) Fe (red squares) and Mn (black circles) at southern coastal Station 16-394. Bottom is at approximately 300m.
Figure 5. Comparison of the vertical profiles of dissolved Fe (dFe), labile particulate Fe (LpFe), and total particulate Fe (TpFe) at Stations 15-24, 16-414, and 16-445 (top panels). Note particulate Fe concentrations are much larger than dissolved, and are shown on bottom x-axis. Bottom panels show the same variables for Mn at the same stations, all values on the top x-axis.
Figure 6. Time series of dissolved Fe and Mn, meteoric water contribution (left y-axis) and mixed layer depth (right y-axis) at Station E in early 2015. Note mixed layer depth is plotted increasing down to be more visually intuitive.

SHORT TITLE FOR PAGE HEADINGS: Iron supply to the Palmer Deep hotspot