1 Title: 2 The relative roles of Modified Circumpolar Deep Water and sediment resuspension in 3 maintaining the phytoplankton blooms above Pennell and Mawson Bank, Ross Sea. 4 5 Author names and affiliations: Mariko Hatta^{1*}, C. I. Measures¹, P. J. Lam^{2,3}, D. C. Ohnemus^{2,4}, Maureen E. Auro², M. 6 M. Grand^{1,5}, K. E. Selph¹ 7 8 ¹School of Ocean and Earth Science and Technology, Department of Oceanography, 9 University of Hawai'i at Manoa, 1000 Pope Road, Honolulu, HI 96822. ² Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic 10 11 Institution, 266 Woods Hole Road, Woods Hole, MA 02543. ³ (now at) Department of Ocean Sciences, University of California, Santa Cruz, 1156 12 13 High St, Santa Cruz, CA 95064 ⁴ (now at) Bigelow Laboratory for Ocean Sciences, East Boothbay, ME, USA. 14 ⁵ (now at) University of Southampton, National Oceanography Centre, European Way, 15 Southampton, UK. 16 17 *Corresponding author 18 mhatta@hawaii.edu; 1-808-956-6632 19 20 Key words (up to 6 key words): 21 Iron; Banks; Ross Sea; Modified Circumpolar Deep Water; Water mixing; Manganese

- 23 Highlights (3-5 highlights, 85 characters, core results):
- 24 Dissolved Fe within the CDW is diluted by mixing with AASW during the formation
- 25 of MCDW in the Ross Sea.
- 26 **•** MCDW was seen above Mawson Bank but not Pennell Bank.
- ♦ A diagenetic input of Fe is seen above Pennell Bank.
- Strong tidal energy over shallow banks brings Fe-rich deep waters to the euphotic
 zone.
- The presence of MCDW above Mawson Bank hinders mixing of dFe into the euphotic
 zone.
- 32

33 Abstract:

34 In order to understand the mechanisms that lead to frequently observed discrete 35 patches of high chlorophyll biomass over Pennell Bank (PB) and Mawson Bank (MB) 36 during the last 16 years in the iron (Fe)-limited high nutrient low chlorophyll waters of 37 the Ross Sea, a research project ("SEAFARERS": Slocum Enhanced Adaptive Fe Algal 38 Research in the Ross Sea) was undertaken during the austral summer, January/February 39 2011. The goal of this project was to determine the chemical/physical/biological 40 parameters of the region and to evaluate whether Fe-enriched Circumpolar Deep Water 41 (CDW), which is known to intrude into the Ross Sea, was a major source of Fe fuelling 42 the observed phytoplankton blooms. Since all of the surface waters of the region have 43 been shown to be Fe-limited, the presence of regular blooms above these banks (which 44 are also Fe-limited) is most likely the result of an enhanced and regular Fe supply to 45 those surface waters.

46 Our dissolved and particulate trace element results showed that the dissolved Fe 47 content of the CDW is actually reduced by on-shelf mixing with Antarctic Surface Water 48 as it transitions into Modified Circumpolar Deep Water (MCDW). Our stations above 49 PB, where the maximum bloom is encountered, showed evidence of diagenetic input of 50 Fe from the sediments into the bottom waters, connected to the strong tidal cycles in this 51 region, with the high dFe values encountered when water flowed south across the large 52 expanse of shallow sediments found on the top of this bank. We saw no evidence of the 53 classically defined MCDW above PB and thus discount the role of CDW/MCDW in 54 promoting the bloom seen here. In contrast, above MB, the site of a smaller persistent 55 bloom, we saw evidence of a relatively strong Fe signal in the bottom waters, associated 56 with MCDW, but no evidence of diagenetic input from the much smaller area of shallow 57 sediments found on this bank. The extremely strong tidal energy in this region is 58 undoubtedly responsible for bringing deeper, Fe-rich waters into the euphotic zone above 59 these banks, but the much stronger vertical density gradient above MB, due to the 60 presence of MCDW, suggests that physical processes are limiting the Fe supply to MB. 61 Thus, ironically, the presence of MCDW maybe hindering the supply of Fe to the surface 62 rather being originally waters. than the source. hypothesized. as

63 **1. Introduction**

64 The Southern Ocean is well-known as a High Nutrient Low Chlorophyll (HNLC) 65 region, but within this low biomass area the Ross Sea continental shelf is one of the most 66 productive areas in the Southern Ocean (Sullivan et al., 1993; DiTullio and Smith, 1996; 67 Smith and Gordon, 1997; Arrigo et al., 1998a; Smith and Cosimo, 2008), and thus is 68 considered as an important oceanic CO₂ sink region (Marinov et al., 2005; Arrigo et al., 69 1998b; Takahashi et al., 2009). The increased biomass seen during iron addition 70 experiments in the Southern Ocean waters (e.g., Martin et al., 1990; Sedwick and 71 DiTullio, 1997) suggests that it is iron, an essential nutrient for phytoplankton growth, 72 that is limiting primary production in the Southern Ocean (Martin et al., 1991; Coale et 73 al., 1996; Sedwick et al., 2000; Boyd, 2002; Coale et al., 2003; 2005).

There are multiple potential iron sources to the Ross Sea, such as dust, sea-ice, icebergs, upwelling of deeper waters and sedimentary input, etc., and these have been discussed by a variety of authors (Martin et al., 1991; Fitzwater et al., 1996; Sedwick et al., 1996; Sedwick et al., 2000; Measures and Vink, 2001; Boyd, 2002; Coale et al., 2005; Sedwick et al., 2011; Measures et al., 2012; Marsay et al., 2014).

79 Seasonal iron limitation has been suggested for the Ross Sea (Sedwick and 80 DeTullio, 1997; Sedwick et al., 2000; Coale et al., 2003; 2005; Bertrand et al., 2007) as a 81 result of the effects of phytoplankton uptake, particle export, and scavenging. However, 82 in a recent study, Sedwick et al. (2011) reported low dissolved Fe (dFe) concentrations 83 (~0.1 nM) in the euphotic zone of the Ross Sea polynya by late spring (November), 84 concluding that the surface waters in the Ross Sea polynya (southern Ross Sea) can 85 become iron depleted even during an early stage of the seasonal phytoplankton bloom. 86 These authors concluded that in order to sustain the high productivity in the Ross Sea, 87 there must be a significant supply of new dFe to surface waters of the polynya during the 88 growing period.

In contrast to the large areas of high chlorophyll biomass in the inshore regions, the offshore regions show only small patches of high chlorophyll biomass (Fig 1). In particular there are discrete blooms that have been occurring above Pennell Bank (PB)

92 and Mawson Bank (MB) at the same time of year from 1998 to 2014 (Kohut et al., this 93 issue). The seasonal persistence of these features also suggests that there should be a 94 continual source of Fe, fuelling phytoplankton blooms above the bank. The dye 95 simulation model of Dinniman et al. (2011) confirmed Circumpolar Deep Water (CDW) 96 intrusions onto the shelf in specific locations primarily determined by the bathymetry 97 (Kilinck and Dinniman, 2010), which then mixes with surrounding water masses to 98 become Modified Circumpolar Deep Water (MCDW, Jackobs and Giulivi, 1998; Gordon 99 et al., 2000; Orsi and Wiederwohl, 2009; Whitworth et al., 2013). In addition, Dinniman 100 et al. (2011) showed there was vigorous mixing of the CDW/MCDW with the surface 101 waters in the Ross Sea. Since CDW contains relatively high levels of dFe compared to 102 the shelf region, this water has been considered as a potential source of Fe fuelling 103 primary production in the Ross Sea (Hiscock, 2004; Peloquin and Smith, 2007).

104 In order to investigate, identify and understand the factors and mechanisms that 105 lead to these patches of higher biomass, a research project ("SEAFARERS", Slocum 106 Enhanced Adaptive Fe Algal Research in the Ross Sea, Kohut et al., 2013) was 107 undertaken during the austral summer (January 2011). The goal of this project was to 108 determine the chemical/physical/biological parameters of the region and to evaluate 109 whether the Fe-enriched CDW was a major source of Fe fuelling the observed persistent 110 phytoplankton blooms above the banks. To achieve this, we determined the distributions 111 of dissolved and particulate Fe, dissolved Mn and dissolved Al at key stations on the 112 shelf to enable us to follow the mixing process of CDW as it transitions into MCDW. A 113 key physical process in the Ross Sea is the strong tidal effect in this region and the tide's 114 effect on mixing processes. Thus, in addition to the normal shipboard sampling program, 115 data from a relocated mooring, as well as gliders, were used to increase the temporal and 116 spatial range of the sampling program (Kohut et al., this issue).

- **117 2. Methods**
- 118 2.1. Sampling

119 2.1.1 Dissolved trace metal samples

Over 180 water samples were collected for trace metal determinations at 15 stations (Fig 1) in the Ross Sea between 17 January and 13 February 2011 as part of the "SEAFARERS" campaign (Slocum Enhanced Adaptive Fe Algal Research in the Ross Sea) aboard the R/V Nathaniel B. Palmer (cruise NBP 11-01). An additional, 12 water samples were collected on 21 February 2011 at station 100 (Fig 1) at the start of the CLIVAR S4P cruise (cruise NBP 11-02) that immediately followed the "SEAFARERS" cruise.

127 Water samples were obtained using a custom-built trace metal (TM) clean rosette 128 consisting of an epoxy painted Al rosette frame containing 12 x 12L GO-FLO bottles 129 (Measures et al., 2008a) and that housed an SBE 911 CTD system which included an 130 SBE 43 dissolved oxygen sensor and a Wet labs FL1 fluorometer. However, due to the 131 oxygen sensor freezing during the cruise, oxygen data are not available. Immediately 132 after each deployment the package was recovered, the tops of the GO-FLO bottles were 133 covered with plastic bags and the bottles removed from the frame and carried into the 134 clean van for sub-sampling. The GO-FLO bottles were pressurized to 10 psi using 0.2 135 μm-filtered compressed air and water samples were filtered through a 0.45 μm pore size 136 acid washed, 47 mm polysulphone filter (Pall Supor 450 P/N 60173) as they were 137 collected into sample bottles. All sub-sampling was undertaken in the clean van using 138 rigorous trace metal protocols. The sampling system and protocols are described in detail 139 in Measures et al. (2008a). Samples obtained with this system and processed in this 140 manner have been shown during the SAFe inter-comparison cruise (Johnson et al., 2007) 141 and the GEOTRACES inter-calibration cruise to produce concentrations of trace metals 142 (Al, Fe and Mn) that are, within analytical uncertainty, identical to those obtained using 143 other currently accepted sampling methodologies for trace elements (i.e., U.S. 144 GEOTRACES sampling protocols, Cutter and Bruland, 2012). Also, this sampling 145 system has been used successfully to collect uncontaminated trace element samples 146 during several projects (e.g., CLIVAR projects: Measures et al., 2008b; Grand et al., 147 2014, 2015a, 2015b; BWZ project: Measures et al., 2013; Hatta et al., 2013).

Filtered seawater samples (0.45 μm pore size) were collected and drawn into acid
 pre-washed 125 ml polymethylpentene bottles after three rinses with sample water; filled

150 sample bottles were stored in polyethylene bags in the dark at room temperature before 151 the shipboard determination. Duplicate samples were also collected and drawn into 152 previously acid-leached 125 mL HDPE bottles after three sample rinses for shore-based 153 determination of dissolved Fe (dFe) and dissolved Mn (dMn) by Inductively Coupled 154 Plasma Mass Spectrometry (ICP-MS).

155 2.1.2 Particulate Fe samples

156 Six-depth profiles of size-fractionated particles analyzed for particulate Fe at 157 selected stations (Stations 14, 55, 70, 35, 24, 7, and 28, shown in Fig 1) were collected by 158 in-situ filtration using modified dual-flow McLane WTS pumps (Ohnemus and Lam, 159 2015). The filter configurations on the two flowpaths were those used on all US 160 GEOTRACES cruises, and consisted of a 51 µm polyester prefilter followed by paired 161 0.8 µm polyethersulfone (PES; Pall Supor800) filters "Supor", and a 51 µm polyester 162 prefilter followed by paired quartz fiber filters "QMA" (Whatman QMA) (Cutter et al., 163 2014; Ohnemus and Lam, 2015). Up to 478 L and 1100 L were filtered through the 164 "Supor" and "QMA" flowpaths, respectively, over the typical 2-3 hour pump time at an 165 initial pumping rate of 8 L/min. A complete filter set sandwiched between 1 µm mesh in 166 perforated polypropylene containers was deployed at each station as a "dipped blank", 167 which functioned as a process and adsorption blank.

168 2.2 Analytical methods

169 2.2.1 Determination of dissolved trace elements

Dissolved trace element determinations were performed on board ship using the filtered sub-samples from the GO-FLO bottles within a few hours of sample collection. Prior to analysis, samples were acidified by adding 125 μ l sub-boiling distilled 6N HCl, and were then microwaved in groups of 4 for 3 minutes in a 900 W microwave oven to achieve a temperature of 60 ± 10°C, to release dFe from complexation in the samples. Samples were allowed to cool to room temperature for at least 1 hour prior to Flow Injection Analysis (FIA). 177 Dissolved Al (dAl), dFe and dissolved Mn (dMn) were determined in the filtered, 178 acidified, microwave-treated subsamples using FIA methods of Resing and Measures 179 (1994) for Al, Measures et al. (1995) for dFe, and Resing and Mottl (1992) for dMn 180 determinations. The detection limit and precision were 0.18 nM and 3.5% at 1.70 nM 181 dAl, 0.12 nM and 3.1% at 1.3 nM dFe, and 0.12 nM and 2.4% at 1.70 nM dMn. 182 However, since most of the results from the shipboard dMn analysis were below the 183 shipboard detection limit, instead we use dMn data from the duplicate samples 184 determined in the more sensitive shore-based ICP-MS at the University of Hawaii in this 185 study.

186 Shipboard data sets have been compared with the ICP-MS data to calculate the 187 FIA system blank for dFe. No detectable blank from either the acid or sample buffer 188 were found for Al. Samples for shore-based ICP-MS determinations for dFe and dMn 189 were filtered on board using identical methods as those for the FIA samples, and were stored in 125 mL LDPE bottles and acidified in the shore lab to 0.024 M with ultrapure 190 191 6N HCl, prior to analysis. Pre-concentration and extraction of samples for the 192 determination of dFe and dMn was performed using a flow injection manifold with an in-193 line micro-column containing 200 mL of Toyopearl AF Chelate-650 M resin following 194 the protocol of Milne et al., (2010). The pre-concentrated samples were analyzed by 195 ICP-MS (Element2, Thermo Scientific) with an Apex-Q (ESI). Detection limits for Fe 196 and Mn were calculated from 3 standard deviations of determinations of replicate ICP-197 MS measurements and were approximately 0.01 nM and 0.05 nM, for Fe and Mn, 198 respectively. Determination of dFe (1.00 ± 0.14 nM, n=10) in the GEOTRACES open 199 ocean reference material (GD) were in good agreement with the inter-laboratory averages 200 reported for these materials (GD = $0.95 \pm 0.05 \mu mol/kg$). Determination of dMn ($0.23 \pm$ 201 0.03 nM, n=10 (GD); 1.30 ± 0.39 nM, n=5 (GS)) in the GEOTRACES open ocean 202 reference material were also in good agreement with the inter-laboratory averages reported for these materials (GD = $0.21 \pm 0.04 \mu mol/kg$, GS = $1.45 \pm 0.17 \mu mol/kg$). 203

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204 **2.2.2 Determination of particulate trace metals**

Separate subsamples of the top Supor filter (the 0.8 - 51 μm size fraction)
 representing 3 - 9% of the filter area (median 13 L equivalent volume filtered) were used

207 to determine the total and leachable concentrations of particulate trace metals. Total 208 digestions were effected with the Piranha method (Ohnemus et al., 2014; Ohnemus and 209 Lam, 2015). Briefly, this two-step digestion first uses a strong oxidizing solution (the 210 Piranha reagent: 3 parts concentrated H_2SO_4 to 1 part concentrated H_2O_2) to completely 211 digest the PES filter and other particulate organic material, followed by a strong acid 212 cocktail (4M each of HNO₃, HCl, and HF) to completely digest the silicate components 213 of suspended marine particles. For acid labile concentrations of particulate trace metals, 214 separate subsamples were leached in 2 mL 1M HCl at room temperature for 24 hours in 215 15 mL centrifuge tubes. Samples were centrifuged at 4100 rpm for 45 minutes, and 1.5 216 mL of supernatant was transferred into a Teflon vial. The cold HCl leach used here is 217 more aggressive than other commonly used weak acid leaches (e.g., Berger et al., 2008), 218 but has the advantage of having been tested on a variety of iron bearing minerals: it has 219 been shown to extract Fe from poorly crystalline Fe(III) oxyhydroxides and a small 220 fraction of some phyllosilicates, but not crystalline Fe(III) oxides (Raiswell et al., 1994).

221 Total digest and leach solutions were dried down at 110 °C and residues were brought back up into solution with 5% HNO₃. The final solution was run at the WHOI 222 223 Plasma facility on a Thermo Element2 HR ICP-MS using a quartz spray chamber 224 introduction system. Matrix suppression and internal drift was corrected using 1 ppb In 225 as an internal standard, and concentrations were quantified using mixed element external 226 standard curves (Ohnemus et al., 2014). The detection limit was defined as three times 227 the standard deviation of all dipped blank filters, and was 2.7 nmol/filter and 9.9 228 nmol/filter for leachable and total particulate Fe (pFe), respectively. For a median 229 volume filtered of 300 L, this is equivalent to detection limits of 9 pM for leachable pFe 230 and 33 pM for total pFe. Repeat determinations of total and leachable pFe had average 231 relative standard deviations of 3% and 10%, respectively.

232 2.3 Ancillary data

In order to understand the detailed water characteristics and biological activity during the cruise, shipboard Acoustic Doppler Current Profiler (ADCP) data, oxygen data, Photosynthetically Active Radiation (PAR) data, fluorescence, and transmissometer data are used in the discussion. However, since there was no PAR sensor or transmissometer sensor attached to the TM rosette and no usable data from the TM rosette oxygen sensor, we use oxygen, PAR, and transmissometer data from the regular hydrographic CTD rosette casts, which were deployed within 2-3 hours of the TM casts. Temperature and salinity records indicated that there was no significant change in water properties between these occupations (data not shown).

ADCP data (units: m/s): In order to identify the surface current and tidal influence of the sampling period, we use the shipboard hull-mounted ADCP "narrowband" instrument (NB150). These data are publicly available at the website <u>http://currents.soest.hawaii.edu/nbpalmer/</u> using the cruise recognition code of "nbp1101".

Fluorescence (units: volts): The raw sensor voltages (0-5 volts) from the Wet
Labs FLRTD-855 (mounted on the TM rosette during each cast) are used in this study.

Transmission (units:%): We use the signal from the C-star transmissometer
(WET Labs, Inc.) mounted on the regular hydrographic CTD rosette to provide insights
into the level of particulate material in the water column at the various stations.

252 Mixed layer depth (units: m): The oceanic mixed layer is defined as the surface 253 layer where the temperature and salinity are vertically homogeneous. In the Southern 254 Ocean, Mixed Layer Depths (MLDs) have previously been defined using criteria based 255 on the change in potential temperature or density with respect to the surface value, (e.g., $\Delta \theta = 0.5^{\circ}$ C, $\Delta \sigma_{\theta} = 0.125 \text{ kg/m}^3$ and $\Delta \theta = 0.2^{\circ}$ C, $\Delta \sigma_{\theta} = 0.03 \text{ kg/m}^3$). In this study, we 256 define the MLDs using the potential density criteria of $\Delta \sigma_{\theta} = 0.03 \text{ kg/m}^3$ from the surface 257 258 value, which has also been shown to provide good agreement between density and 259 oxygen based mixed layers in the Bellingshausen Sea (Castro-Morales and Kaiser, 2012). 260 Calculated MLDs (data from regular hydrography CTD rosette and TM rosette) and the 261 depth of the PAR 1% light level are shown in Table 1 together with selected water property parameters within the MLDs. 262

263 **3. Results and discussion**

264 Here we report the dissolved ($<0.45 \mu m$) Al, Fe, Mn from the trace metal clean 265 rosette sampling system and the particulate (leachable and total) Fe data from the trace 266 metal clean pumping system. All of the trace metal data presented here are available at 267 the Center using U.S. Antarctic Program Data Entry ID: NBP1101. 268 http://gcmd.nasa.gov/KeywordSearch/Metadata.do?Portal=GCMD&MetadataView=Full 269 &EntryId=NBP1101.

270 Potential temperature and salinity data are shown in Fig 2 with selected stations 271 shown in color in order to identify typical water masses found in the study area. The 272 distribution of hydrographic parameters (temperature, salinity, neutral density, 273 fluorescence, silicate, and phosphate) in the section across the basin (red box shown in 274 Fig 1) are shown in Fig 3, and the corresponding dissolved and particulate trace metal 275 distributions are shown in Fig 4. The vertical depth profiles of hydrographic parameters 276 and trace elements at the repeated sampling station located on the western side of PB in 277 Joides Basin and the offshore station are presented in Fig 5 and data from the stations 278 above PB and MB are in Fig 6. Property-property plots of the MCDW (neutral density = $28.0 - 28.27 \text{ kg/m}^3$) are shown in Fig 7. Also, the property-property plots of the AASW 279 above PB (neutral density $\leq 28.00 \text{ kg/m}^3$) are shown in Fig 8. Figures were made using 280 281 Ocean Data View (Schlitzer, 2015). The MLDs at each station are shown in Table 1, and 282 the averaged concentration of each dissolved parameter in the each of the water masses 283 are shown in Table 2. The pFe values (leachable and total) in each water mass are shown 284 in Table 3.

285 **3.1 Water mass characteristics of the Ross Sea**

286 Across the sampling region, the presence of Antarctic Surface Water (AASW), neutral density <28.00 kg/m³ (Orsi and Wiederwohl 2009), is evident in the upper 200 m 287 288 from its high temperature and low salinity. Below 300 m, in the channels between the 289 banks, High Salinity Shelf Water (HSSW, >34.62 psu, Orsi and Wiederwohl 2009) can 290 be seen at Stations 55, 35, 100, 24 and 2 (Fig 3b). Between these water masses lies the 291 MCDW, which results from mixing of the inflowing CDW as it flows southward across the shelf. This MCDW, neutral density 28.00 - 28.27 kg/m³ (Orsi and Wiederwohl 2009; 292 Kohut et al., 2013), can be seen along the western side of PB at 218 - 275 m (Stations 16, 293

24, 41) and along the western side of MB at 150 - 230 m (Station 55). This water mass has a relatively high temperature (-1.3 to -0.6 °C), low salinity (34.52 - 34.55 psu) and low dissolved oxygen (DO; 233 - 250 μ mol/kg, latter not shown in this figure) as a result of the properties of the originating offshore CDW.

298 **3.2 Dissolved and particulate trace metal distributions**

The trace element distributions show large contrasts, with low concentrations in surface waters and higher concentrations towards the bottom (Fig 4). The following sections will focus on each water mass as identified by its physical properties discussed above. We will first look at the characteristics of the two potential mixing partners of CDW, i.e., the surface waters (AASW) and the deeper waters (HSSW), before using this information to describe the evolution of the MCDW on the shelf.

305 3.2.1 Surface Waters (AASW)

306 Within the MLD of the sampling region, dFe ranges from 0.08 - 0.25 nM, 307 leachable pFe from 0.042 - 0.120 nM, total pFe from 0.047 - 0.265 nM, and dMn from 308 0.01 - 0.45 nM (Fig 4f, a, b, and Tables 2 & 3). The persistent patches of high 309 fluorescence (i.e., phytoplankton blooms) discussed in the introduction can be seen at 310 Station 35 and over PB at Stations 7, 61 and 28; these correspond to higher surface 311 temperature, and low silicate and phosphate concentrations (Fig 3a, e, f). There is also an 312 additional, weaker, patch of high fluorescence at Station 48, north of the section, above 313 PB (Table 2).

314 Slightly higher dFe values (0.15 - 0.25 nM) are seen coincident with the higher 315 fluorescence signals (>0.82 volts) at Stations 35, 24, 7, 61, 21 and 28, near PB, with 316 relatively lower dFe values (0.08-0.17 nM) coincident with the lower fluorescence 317 signals (<0.4 volts) at Stations 55, 70, 16, and 41, near MB (Table 2). This suggests that 318 dFe is indeed a factor in controlling phytoplankton growth in the area. Even though the 319 dFe concentrations are higher in the regions of high fluorescence, shipboard Fe-addition 320 incubation experiments strongly suggested that all the surface waters of the region were 321 deficient in dFe (Kustka et al., 2015). Since dFe is limiting in all regions, but some areas 322 have much higher biomass than others, this suggests that there is a dFe supply above the 323 banks where there is enhanced biomass. Using the observed surface water nitrate concentration of ~24 μ M, and by assuming a C:Fe ratio of 10⁵:1 in growing plankton 324 (Measures and Vink, 2001; Sunda and Huntsman, 1995), we calculate that total 325 326 biologically-available Fe values of ~1.6 nM would be needed to fully utilize this amount 327 of nitrate. In addition to the dFe, higher concentrations of leachable and total pFe are 328 seen in the higher fluorescence signal surface waters above PB (Stations 28 and 7, Table 329 3), however these pFe values are still ~ 0.3 nM, far below the estimated requirement. The 330 vertical profiles of pFe and dFe above PB suggest that there is a sedimentary source of 331 leachable pFe and dFe, that we postulate supports the growth of phytoplankton if mixed 332 into the euphotic zone above the banks.

333 In contrast to dFe, higher dMn values (0.35 - 0.45 nM) are seen in surface waters 334 at stations with lower fluorescence signals (Stations 55, 70, 2 and 41), while lower dMn 335 (0.01 - 0.09 nM) is associated with the elevated fluorescence signals (Table 2). The 336 lower dMn values seen in the high fluorescence regions are probably a result of dMn 337 removal from the water column primarily due to surface scavenging by suspended and 338 sinking particles and biological uptake. Although dMn is known to be one of the 339 essential micronutrients for phytoplankton growth (Bruland et al., 1991), and various 340 laboratory experiments have demonstrated limitation of algal growth by Mn deficiency 341 (e.g., Brand et al., 1983; Sunda and Huntsman, 1986), so far there is no convincing 342 evidence for Mn-limitation in ocean waters (e.g., see Martin et al., 1990; Coale, 1991) or 343 in the Ross Sea (Sedwick et al., 2000). Thus, the main dMn removal process is likely 344 surface scavenging in areas with higher particle (i.e., phytoplankton cells) loads.

345 Our measured surface dFe values (0.08 - 0.25 nM, Table 2) are similar to the 346 concentrations in surface water found during summer 1995 (0.18 ± 0.08 nM, Sedwick et 347 al., 2000), and are slightly higher than the recently reported results in open polynya 348 surface waters further to the south of our region $(0.10 \pm 0.05 \text{ nM} \text{ in } 2005-2006 \text{ summer})$ 349 0.06 ± 0.04 nM in 2006 spring, Sedwick et al., 2011; and 0.08 ± 0.07 nM in 2012 350 summer, Marsay et al., 2014). In contrast, our higher (in the low fluorescence region) 351 dMn values (0.35 - 0.45 nM, Table 2) are similar to the 1995 values (0.21-0.22 nM of 352 Sedwick et al., 2000).

353 **3.2 High Salinity Shelf Water (HSSW)**

354 Within the HSSW, a similar enrichment of dAl, dMn and dFe near the bottom of 355 Stations 55, 35, and 24 suggests a common benthic source for these elements, as does the 356 extremely high values of pFe (both leachable and total, Fig 4a, b; Tables 2 & 3) and 357 lower transmission signals (data not shown). High values of dAl, dFe and dMn are also 358 seen at the bottom of Station 100, but there are no pFe data available from this station for 359 comparison. These higher concentrations of dFe and dMn are probably due to the release 360 of pore waters from the sediments by the strong tidal action on the shelf. Support for this 361 idea comes from Marsay et al. (2014), who recently reported a high benthic flux of dFe 362 from the sediments in the southern part of Ross Sea continental shelf during the austral 363 summer 2012.

364 **3.3 Modified Circumpolar Deep Water (MCDW)**

365 In order to understand the evolution of the MCDW as it flows across the shelf, 366 water samples were collected repeatedly at different stages of the tidal cycle at a location 367 in the Joides Basin to the west of PB over an 11-day period (Stations 16, 24, 41, shown in 368 Fig 1). The dFe profiles during all three occupations show a constant but similar value 369 (0.1 - 0.2 nM) from the surface to 200 m in the AASW (Fig 5b). Below the AASW is the depth of the core of the MCDW (shown by the coloured star symbol * at each station and 370 defined by a neutral density range of 28.00 - 28.27 kg/m³, Fig 5). The core of the 371 MCDW, which varies in depth between the occupations as a result of the tidal cycle, is 372 373 coincident with the depth where Fe concentrations start to increase, but the pattern of 374 increase is different between occupations during the tidal cycle. At Stations 16 and 41, 375 dFe values within the deeper core are 0.27 - 0.33 nM, while at Station 24 (with a 376 shallower MCDW core) dFe values continually increase from 0.27 nM at 220 m to 0.64 377 nM at the bottom where HSSW is found (>34.62 psu, Fig 5d). The end member CDW 378 was sampled at the offshore Station 14, where dFe values of 0.33 - 0.34 nM were 379 measured at 400 - 500 m depth (Fig 5b and Table 2).

The shipboard ADCP data during the sampling period of each sampling station (~2 hours) shows the importance of the relative motion of the water across the shelf.

382 There was southward (onshore) flow during the occupation of Stations 16 (-0.32 \pm 0.03 383 m/s) and 41 (-0.15 \pm 0.05 m/s) and northward (offshore) flow during the occupation of 384 Station 24 ($+0.12 \pm 0.04$ m/s). These flow patterns suggest that the deepwater increase in 385 dFe value at Station 24 is from outflowing HSSW shelf waters, which were enriched 386 from benthic sources further south driven by strong tidal processes. The HSSW present 387 at the base of Stations 16 and 41 is much more dilute in dFe, with lower salinity and 388 higher temperatures corresponding to a very small increase in dFe in the bottom-most 389 samples. In contrast, at Station 16, there is a higher dFe value in the MCDW compared 390 to Station 41, which corresponds to stronger onshore flow of the dFe-enriched CDW 391 source (Fig 5b).

MCDW is also seen in the deeper channels at Stations 55, 35, 100, 28, the inner shelf at Station 2, and on top of MB at Station 70. As we will argue below, the relative amount of dFe in the MCDW at these stations appears to be mainly controlled by how much mixing the original CDW has undergone.

396 We will use water mass properties to examine the origin of the trace metal signals 397 in the MCDW. Property-property plot of salinity and potential temperature (within the 398 neutral density range of MCDW) suggests that the formation of MCDW is by mixing the 399 CDW end member with a low salinity end member, i.e., ASSW rather than higher salinity 400 HSSW (Fig 7a). This concept is supported by the salinity vs. Si plot, which also 401 indicates a low Si, low salinity ASSW source rather than the higher Si, higher salinity 402 HSSW (Fig 7b). Similarly, the dFe vs. salinity plot also shows a low dFe mixing partner 403 for the CDW rather than the high dFe HSSW source (Fig 7c). In addition, the dAl and 404 dMn show this same mixing series, but less clearly (Fig 7d, e). Thus, the formation of 405 MCDW from CDW results in a decrease of its dFe content, thus limiting its ability to 406 support biological production. The plot of dFe and dMn in the MCDW (Fig 7f) also 407 confirms the end member mixing series between the high Fe, low Mn CDW and the low 408 Fe, high Mn AASW. Since the Fe and Mn in the AASW probably have a similar source, 409 the fractionation between these two tracers is presumably a result of the shorter residence 410 time of dFe compared to that of dMn in the AASW.

411 In contrast, the leachable pFe values of MCDW (0.93 nM at 230 m at Station 55, 412 and 1.01 nM at 210 m at Station 24, Table 3) are one order of magnitude higher than 413 those in the CDW (e.g., 0.075 nM at offshore Station 14). Additionally, the total pFe 414 values of MCDW (2.75 nM at Station 55 and 3.07 nM at Station 24) are one order of 415 magnitude higher than total pFe in the CDW (0.213 nM at Station 14). This suggests that 416 the MCDW is gaining pFe when it flows onto the shelf, but the dFe is not changing 417 significantly simultaneously. In contrast, the dMn value of MCDW (0.34 - 0.58 nM) is 418 higher than in the CDW (0.11 nM). The opposite behavior of these two dissolved 419 components is consistent with the MCDW being a mixture between the high Fe, low Mn 420 CDW and a low Fe, high Mn AASW (Fig 7c, d, f and Table 2). Also, this suggests that 421 this MCDW is probably not mixed with the HSSW that contains the highest dFe values at 422 Station 24 in the trough on the western side of PB.

423 **3.4 The waters above Pennell Bank**

Repeat water samples were collected at one station above PB (Stations 7 and 61) 18 days apart and samples were also obtained at Station 48 located to the north of these stations within the same period (Fig 6). As mentioned before, at Stations 7 and 61, the slightly higher dFe (0.15 nM and 0.25 nM, respectively, shown in Table 2) were seen coincident with higher fluorescence signals (1.73 and 1.66 volts, respectively). In contrast, the lower dFe values (0.13 nM) were seen in the upper 50 m at Station 48 where there was a relatively low fluorescence signal (0.48 volts).

431 At each of these stations, the dissolved trace element signals are higher below 170 432 m than in the surface waters, suggesting a benthic input (Fig 6b, c). Below 170 m, 433 Station 7 shows constant dFe (0.22 ± 0.01 nM) and dMn (0.37 ± 0.03 nM) values, while 434 Station 48 (dFe = 0.22 to 0.27 nM; dMn = 0.50 to 0.70 nM) and Station 61 (dFe = 0.20 to 435 0.36 nM; dMn = 0.69 to 0.90 nM) show gradual increases from ~ 170 m to the bottom 436 (Fig 6b). These features, however, are more pronounced at Station 61 and 48 than at 437 Station 7. Interestingly, shipboard ADCP data during each sampling period (averaged 438 over ~ 2 hours) shows northward flow (off shelf) during the occupation of Station 7 439 $(+0.14 \pm 0.03 \text{ m/s})$, while there is no strong flow during the occupation of Station 48 (-440 0.042 ± 0.04 m/s) and Station 61 (+0.001 ± 0.04 m/s). Thus, during the occupation of 441 Station 7, under tidal influence, the deepest waters were moving northward on to the PB 442 from deeper areas to the south. In contrast, during the occupation of Stations 48 and 61, 443 the tide was fairly slack, i.e., little motion, but prior to the sampling the water had been 444 moving south across the shallow area of Pennell Bank. It thus seems from our profiles 445 that when the bottom waters move south across the shallower parts of the bank dissolved 446 Fe and Mn are added to the water column. However, when that water moves north onto 447 the bank, it has not had a significant benthic input before reaching the southern edge of 448 We also see evidence for the likely process for this input in the the bank. 449 transmissometer signals, which show the presence of a much higher particulate load in 450 the bottom waters at Stations 48 and 61 than at Station 7 (Fig 6e). In addition, the 451 salinity below 150 m at Station 48 is very uniform (Fig 6d), suggesting that there maybe 452 topographically-induced mixing of the bottom waters in this region to the north of the 453 location of Stations 7 and 61. While we do have total and leachable pFe from Station 7 454 showing increases in both loads towards the sediment interface, we do not have 455 equivalent data from Stations 48 and 61. Other evidence is that the deepest water above the shelf has neutral densities $(27.99 - 28.03 \text{ kg/m}^3)$ that are less than, or at the very edge 456 of, the definition of the classic MCDW ($28.00 - 28.27 \text{ kg/m}^3$), and thus we conjecture that 457 458 this water is the densest part of the AASW, rather than the most dilute form of MCDW. 459 In this regard, we note that the plots of dFe vs. salinity within this water mass are above 460 the mixing line connecting CDW and AASW (Fig 8c). This result implies that the 461 elevated Fe seen above the bank is not a result of MCDW mixing into AASW, but a local 462 diagenetic imprint. The dMn values in the bottom waters are similar to those seen along 463 the CDW-AASW mixing line (Fig 8d), which also suggests that the origin of the Mn 464 enrichment in the AASW is from this diagenetic input. The difference between the 465 relative enrichment of the Mn and Fe is, therefore, likely a result of the shorter residence 466 time of Fe in the water column compared to the Mn.

467 **3.5** The waters above Mawson Bank and comparison to Pennell Bank

In contrast to PB, there is a distinct signal of MCDW at Station 70 above MB between 150 m and the bottom at 255 m (neutral density $28.04 - 28.06 \text{ kg/m}^3$). Within this water mass, we see dFe of 0.28 nM (Table 2), similar to that seen at the repeat 471 stations in the Joides Basin along the western side of PB. However, we do not see any 472 increase in dFe at the very bottom of the profile, suggesting either a lack of diagenetic 473 input or its masking by the relatively elevated dFe present in the MCDW (Fig 6b). 474 Although there appears to be a greater potential supply of dFe in the deeper water column 475 above MB than PB, and a greater potential supply of leachable pFe (Fig 6f), the biomass 476 accumulation is greatest above PB. If, as mentioned earlier, all of the surface waters of 477 the region are Fe-limited, then this suggests that the rate at which these deep supplies of 478 dFe are reaching the euphotic zone must be the factor controlling biological processes in 479 the surface waters. We note that the density gradient in the water column above MB is 480 much greater than that above PB, largely as a result of the presence of more salty MCDW 481 above MB. We suggest that it is this greater density gradient that inhibits vertical mixing 482 of the waters, thus limiting the supply of dFe and pFe to the surface waters of MB. In 483 contrast, the water above PB is comprised of AASW and has much smaller salinity 484 gradients, so presumably experiences less hindrance to vertical mixing.

485 **4.** Conclusion

Dissolved Fe (dFe) values within MCDW (neutral density of 28.00 - 28.27 kg/m³) to the west of PB during different stages of the tidal cycle show that the dFe content within the CDW is diluted by AASW during its evolution into MCDW.

The bottom waters above PB, with neutral densities of 27.99 - 28.03 kg/m³, are less than or at the very edge of the definition of the classic MCDW. The bottom waters, however, show a diagenetic input of Fe and Mn as a result of tidal mixing and topographic forcing, over the large area of shallow sediments on this bank. This input is most pronounced when the water has flowed across the bank from the north rather than when it enters from the south.

In contrast, the bottom water above MB (neutral densities of 28.04 -28.06 kg/m³) has a sizeable supply of dFe and pFe associated with the presence of MCDW, but there does not appear to be a diagenetic input into the deep waters here.

498 The fact that there is less biomass in surface waters, but more dFe in deep waters 499 above MB, compared to more biomass in surface waters, but less dFe in deep waters above PB, suggests that there is more limited upward mixing of deep waters above MB
(and thus less upward mixing of dFe) as a result of the greater density gradient from salty
MCDW in the water column on this bank. Thus, ironically, MCDW may be hindering
the supply of Fe to the surface waters, rather than being the source of this limiting micronutrient, as originally hypothesized.

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718 Figures and Tables

Figure 1. Map of sampling stations in the Ross Sea during the 2011 SEAFARERS cruise and a sampling station (Station 100) during the subsequent CLIVAR S4P cruise. The sampling stations are shown with blue circles, adjacent to the station's numbers. The red box encompasses the stations that are a section across Drygalsky Basin (DB), Mawson Bank (MB), Joides Basin (JB), Pennell Bank (PB), and Glomar Challenger Basin (GBC). The insert (top left) shows a composite satellite image of Chl-*a* from MODIS during this expedition (blue is lower values and red is higher values of Chl-*a* fluorescence).

726 Figure 2. Potential temperature and salinity data from all stations occupied, with selected 727 stations shown in color in order to identify the typical water masses found. Offshore 728 station (Station 14, red circles), one station at the western side of Pennell Bank (Station 729 16, green squares), the inner shelf with MCDW water (Station 2, blue cross), and inner 730 shelf (Station 3, black circles) with less pronounced MCDW features. Station 48 (purple 731 circles) is located above Pennell Bank. Abbreviations: AASW = Antarctic Surface 732 Water; CDW = Circumpolar Deep Water; MCDW = Modified Circumpolar Deep Water; 733 HSSW = High Salinity Shelf Water.

Figure 3. Distributions of water properties in the section above Pennell and Mawson banks (stations shown in Figure 1) as a function of longitude. (a) Temperature (°C), (b) Salinity (psu), (c) Neutral Density (kg/m³), (d) Fluorescence (volts), (e) Silicate (μ M), and (f) Phosphate (μ M).

Figure 4. Distributions of trace elements in the section above Pennell and Mawson
banks (stations shown in Figure 1) as a function of longitude. (a) Leachable particulate Fe
(pFe, nM), (b) Total pFe (nM), (c) Percent of leachable pFe (%), (d) dissolved Al (dAl,
nM), (e) dissolved Mn (dMn, nM), and (f) dissolved Fe (dFe, nM).

Figure 5. Vertical depth (m) profiles of various parameters from the repeated stations on
the western side of Pennell Bank (Stations 24, 24, and 41) and the offshore station
(Station 14). (a) temperature (°C), (b) dissolved Fe (dFe, nM), (c) dissolved Mn (dMn,
nM), (d) salinity (psu), (e) leachable pFe (nM), (f) total pFe (nM). The depth of the core

of the MCDW is shown by the star (*) symbol on the profile and its colour is the same asthe station's data colour.

Figure 6. The vertical depth (m) profiles of parameters from the repeated stations at the
top of Pennell Bank (Stations 7, 61, and 48). (a) temperature (°C), (b) dissolved Fe (dFe,
nM), (c) dissolved Mn (dMn, nM), (d) fluorescence (volts), (e) transmission (%), (f)
leachable pFe (nM).

Figure 7. Property-property plots (salinity vs. various properties and dFe vs. dMn) of the MCDW and CDW (neutral density = $28.0 \sim 28.27 \text{ kg/m}^3$), at the repeated stations along the western side of Pennell Bank (Stations 16, 24, 41; all MCDW stations), the inshore station (Station 3) that is less modified with MCDW water, and offshore station (Station 14, CDW station). Salinity is plotted as a function of: (a) potential temperature, (b) silicate (μ M), (c) dFe (nM), (d) dMn (nM), and (e) dAl (nM). Finally, (f) dFe is plotted as a function of dMn from the MCDW stations.

Figure 8. Property-property plots of water with neutral density $<28.00 \text{ kg/m}^3$ (AASW), at stations above Pennell Bank (Stations 7, 61, 48). Salinity is plotted as a function of: (a) potential temperature, (b) silicate (μ M), (c) dFe (nM), (d) dMn (nM), (e) dAl (nM). (f) dFe as a function of dMn. The red line in each box shows the mixing line for MCDW formation between CDW and its AASW mixing partner (as plotted in Fig 7).

Table 1. Station locations (refer to Fig 1), and Mixed Layer Depth (MLD, db), maximum
fluorescence depth (Max. FL depth, m), and the depth of 1% PAR. The MLD and 1%
PAR depth from the hydrographic rosette are indicated with a "*" in their column
headers.

Table 2. Station water mass characteristics. Shown are station locations, averaged dFe
and dMn (nM), fluorescence signals (FL, volts), and the density ranges for each water
mass. A question mark in the Water Mass column indicates that the identity of the water
masses is not clear from the available data. Abbreviations: AASW = Antarctic Surface
Water; CDW = Circumpolar Deep Water; MCDW = Modified Circumpolar Deep Water;
MB = Mawson Bank; PB = Pennell Bank, DB = Drygalsky Basin; JB = Joides Basin;
GBC = Glomar Challenger Basin.

Table 3. The leachable and total pFe concentrations (L-pFe and T-pFe, respectively, nM)
in the water masses at stations occupied in the Ross Sea, with the station regions
indicated. Abbreviations: AASW = Antarctic Surface Water; CDW = Circumpolar Deep
Water; MCDW = Modified Circumpolar Deep Water; MB = Mawson Bank; PB =
Pennell Bank, DB = Drygalsky Basin; JB = Joides Basin; GBC = Glomar Challenger
Basin.



Fig.1

















792 Table 1. Station locations (refer to Fig 1), and Mixed Layer Depth (MLD, db), maximum fluorescence depth (Max. FL depth, m), and

the depth of 1% PAR. The MLD and 1% PAR depth from the hydrographic rosette are indicated with a "*" in their column headers.

Location	Station #	Longitude	Latitude	MLDs [db]	Max. fluorescence depth [m]	MLDs*	1% PAR depth [m]*
Offshore	14	178.00	-74.50	40.00	10-46	28	43
Offshore	30	178.75	-74.20	19.00	20-50	22	24
DB	55	173.17	-73.08	74.00	0-74	55	50
above MB	70	174.00	-73.35	49.00	60-90	43	65
JB	35	174.83	-73.58	33.00	24-48	33	36
JB	100	175.83	-73.88	40.00	20-70	No data	No data
JB	16	176.67	-74.13	32.00	62-104	31	82
JB	24	176.66	-74.14	25.00	23-58	14	58
JB	41	176.67	-74.13	38.00	21-40	37	66
above PB	7	178.00	-74.50	30.00	22-47	41	22
above PB	61	178.00	-74.50	40.00	10-46	51	23
above PB	48	178.75	-74.20	40.00	49-61	19	61
GBC	28	179.50	-74.87	44.00	10-44	40	28
Inner shelf	2	174.00	-75.19	43.00	33-60	32	No data
Inner shelf	3	178.52	-76.16	44.00	10-45	40	54
Inner shelf	21	177.00	-75.75	39.00	10-30	44	24

797	Table 2. Station water mass characteristics. Shown are station locations, averaged dFe and dMn (nM), fluorescence signals (FL,
798	volts), and the density ranges for each water mass. A question mark in the Water Mass column indicates that the identity of the water
799	masses is not clear from the available data. Abbreviations: AASW = Antarctic Surface Water; CDW = Circumpolar Deep Water;
800	MCDW = Modified Circumpolar Deep Water; MB = Mawson Bank; PB = Pennell Bank, DB = Drygalsky Basin; JB = Joides Basin;
801	GBC = Glomar Challenger Basin.

Water mass	Region	Station #	dFe (nM)	dMn (nM)	FL (volts)	Neutral Density (kg/m ³)
	Offshore	14	0.16	0.24	0.39	
	DB	55	0.08	0.45	0.39	
	above MB	70	0.16	0.35	0.37	
	JB	35	0.18	0.08	0.92	
	JB	100	0.20	0.11	0.57	
	JB	16	0.17	0.1	0.31	
	JB	24	0.19	0.17	0.81	
AASW within	JB	41	0.11	0.36	0.4	
MLDS	above PB	48	0.13	0.17	0.48	
	above PB	7	0.15	0.05	1.73	
	above PB	61	0.25	0.01	1.66	
	GBC	28	0.16	0.05	1.42	
	Inner shelf	2	0.13	0.35	0.4	
	Inner shelf	3	0.19	0.13	0.51	
	Inner shelf	21	0.18	0.01	1.46	
CDW	Offshore	14	0.36	0.11		28.00-28.27
	DB	55	0.26	0.37		28.02-28.12
MCDW	above MB	70	0.28	0.37		28.03-28.08
WICDW	JB	35	0.26	0.54		28.03-28.08
	JB	100	0.26	0.42		28.03-28.08

	JB	16	0.30	0.34	28.03-28.20
	JB	24	0.22	0.49	28.05-28.19
	JB	41	0.24	0.46	28.03-28.14
	above PB	61	0.28	0.74	28.00-28.03
	above PB	48	0.24	0.53	27.99
	above PB	7	0.23	0.37	28.00-28.03
MCDW	GBC	28	0.22	0.39	28.00-28.15
MCDW	Inner Shelf	2	0.26	0.58	28.04-28.10
	Inner Shelf	3	0.21	0.73	28.00-28.06
	Inner Shelf	21	0.31	0.51	28.01-28.06
	DB	55	0.25-0.53	0.44-0.66	
HSSW (>34.62)	above MB	35	0.38-0.39	0.47-0.56	
	JB	100	0.26-0.56	0.34-0.79	
	JB	24	0.47-0.64	0.55-0.89	
	JB	41	0.36	0.78	
	Inner Shelf	2	0.48-0.76	1.01-1.44	

804	Table 3. The leachable and total pFe concentrations (L-pFe and T-pFe, respectively, nM) in the water masses at stations occupied in
805	the Ross Sea, with the station regions indicated. Abbreviations: AASW = Antarctic Surface Water; CDW = Circumpolar Deep Water;
806	MCDW = Modified Circumpolar Deep Water; MB = Mawson Bank; PB = Pennell Bank, DB = Drygalsky Basin; JB = Joides Basin;
807	GBC = Glomar Challenger Basin.

Water mass	Region	Station #	L-pFe (nM)	T-pFe (nM)
	offshore	14	0.079	0.169
AASW	DB	55	0.073	0.166
	above MB	70	0.054	0.095
	JB	35	0.045	0.053
	JB	24	0.042	0.047
	above PB	7	0.12	0.313
	GBC	28	0.101	0.387
CDW	offshore	14	0.075	0.213
MCDW	DB	55	0.93	2.75
	above NB	70	0.99	3.35
	JB	24	1.01	3.07
	above PB	7	0.72	2.76
HSSW	DB	55	2.68	8.03
	JB	35	2.28	8.76
	JB	24	2.15	6.84