

Influence of iron, cobalt, and vitamin B₁₂ supply on phytoplankton growth in the tropical East Pacific during the 2015 El Niño

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Key points

- Iron, cobalt and vitamin B₁₂ amendments were performed in the Equatorial Pacific/Peru upwelling zone at the onset of the 2015 El Niño
- The El Niño Peru upwelling had residual nitrate and exhibited recovery from community-level iron stress following iron amendment
- Mean chlorophyll was enhanced in response to combined iron and cobalt/ B₁₂ amendment over iron only but was not statistically significant

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Abstract

Iron (Fe), cobalt (Co), and vitamin B₁₂ addition experiments were performed in the eastern Equatorial Pacific/Peruvian upwelling zone during the 2015 El Niño event. Near the Peruvian coastline, apparent photosystem II photochemical efficiencies (F_v/F_m) were unchanged by nutrient addition and chlorophyll-a tripled in untreated controls over two days, indicating nutrient replete conditions. Conversely, Fe amendment further away from the coastline in the high nitrate, low Fe zone significantly increased F_v/F_m and chlorophyll-a concentrations. Mean chlorophyll-a was further enhanced following supply of Fe+Co and Fe+B₁₂ relative to Fe alone, but this was not statistically significant; further offshore, reported Co depletion relative to Fe could enhance responses. The persistence of Fe limitation in this system under a developing El Niño, as previously demonstrated under non-El Niño conditions, suggests that diminished upwelled Fe is likely an important factor driving reductions in offshore phytoplankton productivity during these events.

Index terms (5)

1. 4855 Phytoplankton
2. 4845 Nutrients and nutrient cycling (0470, 1050)
3. 4875 Trace elements (0489)
4. 0480 Remote sensing
5. 4522 ENSO (4922)

Keywords (6)

Phytoplankton, iron, cobalt, vitamin B12, El Niño, Equatorial Pacific

1. Introduction

High levels of phytoplankton productivity in the upwelling regions of the Equatorial Pacific and Peru margin mitigates major CO₂ outgassing [Chavez *et al.*, 1999], lead to emissions of other climate-relevant gases [e.g., Andreae and Raemdonck, 1983; Arevalo-Martínez *et al.*, 2015], and fuel substantial fisheries [e.g., Bakun and Weeks, 2008]. The processes regulating phytoplankton growth in these waters are therefore important to resolve. This is particularly pertinent if periodic high magnitude changes in environmental forcing from the El Niño Southern Oscillation (ENSO) cycle are further modulated by ongoing anthropogenically-induced reductions in seawater pH, lowered oxygen concentrations, altered nutrient inputs, and stratification-driven changes in light intensities [Chavez *et al.*, 1999; Capone and Hutchins, 2013].

The potential for Fe-limited growth conditions in this region has been demonstrated by Fe enrichment experiments and via comparison of dissolved Fe concentrations, chlorophyll-a biomass, phytoplankton fluorescence characteristics, and molecular Fe stress signatures [Martin *et al.*, 1994; Hutchins *et al.*, 2002; Eldridge *et al.*, 2004; Bruland *et al.*, 2005; DiTullio *et al.*, 2005]. The possible role of cobalt (Co) in (co-)limiting part of the extant phytoplankton community has also been predicted for this region [Saito *et al.* 2004; Hawco *et al.*, 2016]; furthermore this has been demonstrated directly in the Costa Rica Dome further to the north [Saito *et al.*, 2005]. Co substitutes for zinc (Zn) in carbonic anhydrase in eukaryotic cells [Yee and Morel, 1996], is a metal center in vitamin B₁₂ [Morel *et al.*, 2003], and has other probable roles in phosphatases, acyltransferases and hydratases [e.g., Martinez *et al.*,

2017; Saito *et al.*, 2017]. Multiple definitions of ‘co-limitation’ exist [Saito *et al.*, 2008], but it is here tested as a situation where both Fe and Co (or B₁₂) have been simultaneously depleted such that only supplying both in combination results in a statistically significant biomass growth response [Browning *et al.*, 2017]. Serial limitation is defined as the sequential biomass enhancement resulting from supplying both the primary (or proximally) limiting nutrient and the next most deficient nutrient [Moore *et al.*, 2013; Sperfeld *et al.*, 2016; Browning *et al.*, 2017].

In an attempt to clarify the potential influences of Fe, Co and vitamin B₁₂ (hereafter referred to simply as B₁₂) on phytoplankton chlorophyll-a biomass and photophysiological characteristics in Equatorial Pacific and Peru upwelling waters, we conducted five short duration (41–45 h) Fe, Co, Fe+Co, and supplementary Fe+B₁₂ amendment experiments on a research cruise in October 2015. Our experimental testing for limiting nutrients coincided serendipitously with the 2015/6 El Niño conditions, further allowing us to place our results within the context of physical and chemical anomalies observed on the same research cruise [Stramma *et al.*, 2016], and in the satellite record.

2. Materials and Methods

Experiments were conducted in October 2015 on cruise SO243 (RV Sonne; Fig. 1). Seawater was collected from a trace-metal-clean towed sampling device at 1–2 m depth linked to a Teflon bellows pump [e.g., Browning *et al.*, 2014, 2017]. Mixed layer depths (MLDs) were calculated using water column density derived from conductivity-temperature-depth (CTD) profiles and a 0.125 kg m⁻³ threshold criterion [de Boyer Montegut *et al.*, 2004]. Satellite data were downloaded from the NASA ocean color website (<https://oceancolor.gsfc.nasa.gov>; all products 9 km resolution reprocessing version R2014.0). Aqua MODIS chlorophyll-a concentrations performed better than VIIRS for match-ups with in situ high performance liquid chromatography (HPLC) concentrations (MODIS: R²=0.83, RMSE=0.25; VIIRS: R²=0.82, RMSE=0.43), and data from this sensor was therefore used for further analyses. Temporally overlapping, average chlorophyll-a concentrations for the Peru shelf were offset between different sensors (see Fig. S1), showing generally much lower values for SeaWiFS and VIIRS as compared to MODIS. Multivariate ENSO Index (MEI) time series (characterizing El Niño intensity) were downloaded from NOAA (<http://www.esrl.noaa.gov/psd/enso/mei/table.html>).

Incubation experiments followed a protocol used in several previous expeditions [e.g., Browning *et al.*, 2014, 2017; Ryan-Keogh *et al.*, 2013]. Briefly, 18 × 1 L acid-washed polycarbonate bottles were filled following a procedure distributing continuously flowing unfiltered seawater from the trace-metal-clean sampling device across all bottles. Treatment bottles were spiked with 2 nmol L⁻¹ Fe, 2 nmol L⁻¹ Co, Fe+Co, and Fe+B₁₂ (B₁₂ concentration of 100 pmol L⁻¹). Fe and Co spikes were made up from 99+% purity salts in acidified deionised water (Milli-Q, Millipore) (FeCl₃, ACROS Organics; CoCl₂, Carl Roth) and the B₁₂ spike solution (Cyanocobalamin; Carl Roth) was passed through a column of a prepared cation exchange resin (Chelex 100) to remove trace metal contamination [Price *et al.*, 1989]. Treatments were conducted in triplicate and accompanied by a set of unamended controls. Bottles were incubated in on-deck incubators shaded to ~30% surface irradiance via blue screen filters (Lee filters, type ‘Blue Lagoon’) and maintained at temperatures of surface waters at the time of cruising by continuous flushing from the ship’s underway seawater supply system.

Chlorophyll-a concentrations were determined fluorometrically using a calibrated fluorometer (Turner Designs, Trilogy) after extraction of pigment from GF/F filters (100 mL seawater filtered) in 90% acetone after 12–24 h in a dark -20°C freezer [Welschmeyer, 1994]. Quantification of extracted phytoplankton pigments (1.1–3.4 L seawater samples filtered onto Whatman GF/F filters, flash frozen and stored at -80°C) was performed via HPLC following Barlow *et al.* [1997] with modifications described in Taylor *et al.* [2011]. Phytoplankton groups were derived from phytoplankton pigments as described in Booge *et al.* [2018].

Phytoplankton photophysiological measurements were performed using a FASTOcean Fast Repetition Rate fluorometer (FRRf) in bench top mode with an integrated FASTact laboratory system (Chelsea Technologies Ltd). Single acquisitions were performed using $100 \times 1 \mu\text{s}$ blue excitation flashes and data were fit using the model of Kolber *et al.* [1998] within the manufacturers software (FASTPro8). Blanks (0.2 μm syringe-filtered samples) were typically run for one replicate per treatment and blank fluorescence was subtracted from F_o and F_m before calculation of $F_v/F_m = (F_m - F_o)/F_m$.

Seawater samples for dissolved trace element analysis were collected in acid-washed 125 mL low-density polyethylene (LDPE) sample bottles (Nalgene), filtered inline using a 0.8/0.2 μm AcroPak1000TM (Pall) filter capsule. Samples were acidified with ultra-pure hydrochloric acid (UpA grade, Romil) to pH 1.9 for >6 months, subject to 4 hour UV irradiation in 30 mL fluorinated ethylene propylene (FEP) bottles, pre-concentrated on a modified seaFAST system (Elemental Scientific Inc) and then analyzed using an Element XR inductively coupled plasma-mass spectrometer (ICP-MS, Thermo Finnigan) [Rapp *et al.*, 2017]. Isotope dilution and standard additions were used to quantify Fe and Co respectively. Manifold and buffer blanks were determined and subtracted from analyzed concentrations as described in Rapp *et al.* [2017]—Fe buffer blank: $0.024 \text{ nmol L}^{-1}$ + manifold blank: $0.0334 \pm 0.0044 \text{ nmol L}^{-1}$ ($n=17$); Co buffer blank: $0.001 \text{ nmol L}^{-1}$ + manifold blank: $0.0021 \pm 0.0007 \text{ nmol L}^{-1}$ ($n=17$). Analyzed concentrations were validated via good agreement with certified reference material (Table S1). Macronutrient samples were analyzed on-ship using a QuAAtro autoanalyzer (Seal Analytical), as described by Stramma *et al.* [2016].

3. Results and Discussion

3.1 Initial conditions

Cruise dates were at the onset of the 2015/6 El Niño: MEI was near the maximum observed for this event (October 2015 MEI=2.3 cf. event maximum in August 2015=2.5), with positive surface temperature anomalies throughout the cruise region (Fig. 1b; Stramma *et al.*, 2016). Bioassay experiments were conducted in three distinct oceanographic regimes (Figs 1, S2, S3; Table 1): (i) Experiment 1: Warm (26.2°C) equatorial waters with depleted nitrate ($0.06 \mu\text{mol L}^{-1}$), 21 m MLD, and a relatively low chlorophyll-a concentration (0.20 mg m^{-3}), with diagnostic pigments suggesting dominance of cyanobacteria (both *Prochlorococcus* and *Synechococcus*) and haptophytes; (ii) Experiments 2, 4, and 5: cooler Humboldt Current waters ($18.0\text{--}22.3^{\circ}\text{C}$) with residual nitrate ($7.46\text{--}26.0 \mu\text{mol L}^{-1}$), MLDs $\sim 20\text{--}33.8 \text{ m}$, and elevated chlorophyll-a ($0.33\text{--}1.62 \text{ mg m}^{-3}$) and diagnostic pigments suggesting dominance of diatoms, haptophytes, and chlorophytes; (iii) Experiment 3: Peruvian shelf waters with elevated nitrate concentrations ($20.3 \mu\text{mol L}^{-1}$), shoaled MLDs ($\sim 13 \text{ m}$), and an enhanced chlorophyll-a concentration (4.26 mg m^{-3}) with diagnostic pigments suggesting dominance of diatoms and chlorophytes.

3.2 Spatial patterns of Fe limitation

Fe stress at experimental sites was evaluated via F_v/F_m changes following incubation of seawater with added Fe, with increases interpreted to reflect coupling of energetically ‘detached’ light harvesting complexes with PSII reaction centers [Behrenfeld and Milligan, 2013; Macey *et al.* 2014]. Associated increases in chlorophyll-a were interpreted as representing proximal limitation of biomass accumulation by Fe availability. Micronutrient amendment in Experiment 1 resulted in no statistically significant F_v/F_m or chlorophyll-a increases over control bottles (Fig. 2a, f), suggesting the community was not proximally Fe/Co/B₁₂ stressed/limited [Browning *et al.*, 2014, 2017; Ryan-Keogh *et al.*, 2013]. This contrasts with previous experiments conducted nearby. Both Martin *et al.* [1994] and Hutchins *et al.* [2002] reported proximal Fe limitation of phytoplankton communities at nearby locations (Fig. 1a) in the same season (September–October), and Saito *et al.* [2005] found Fe-Co co-limitation further to the north in the Costa Rica upwelling dome. In all three previous studies residual nitrate was present (~3.5–10.8 $\mu\text{mol L}^{-1}$), whereas at our experimental site nitrate was depleted (0.06 $\mu\text{mol L}^{-1}$; Table 1), which suggested the site was proximally N-limited or possibly N-Fe co-limited [Browning *et al.*, 2017; Saito *et al.*, 2014; DiTuillio *et al.*, 1993; Behrenfeld *et al.*, 2006].

Although the prevalent El Niño conditions appeared to induce near-cessation of the Equatorial Undercurrent upwelling [Stramma *et al.*, 2016], which could be hypothesized to have reduced supply rates of waters with low Fe:N ratios to the site of Experiment 1, nitrate concentrations at this site from the World Ocean Atlas (WOA) climatology show depletion to <2.9 $\mu\text{mol L}^{-1}$ from July–January (0.76 $\mu\text{mol L}^{-1}$ in October). Surface seawaters in these months are warmer and fresher, with an altered surface ocean current direction (Fig. S3). Therefore, whilst nitrate depletion was slightly accentuated beyond climatological averages during our El Niño occupation, observed differences in responses to Fe amendment in our Experiment 1 and previous studies probably originate primarily from relatively subtle geographic position within the strong regional nitrate gradient [Fig. 1a inset; Fig. S3; Martin *et al.*, 1994; Hutchins *et al.*, 2002].

The one experiment conducted near the Peruvian coastline (Experiment 3; Fig. 2c, h) showed no significant F_v/F_m or chlorophyll-a response to Fe amendment relative to controls (alone or in combination with Co/B₁₂). This suggested that Fe availability was neither stressing the initial phytoplankton community nor limiting chlorophyll-a biomass accumulation. This was consistent with the relatively high dissolved Fe concentrations measured in initial experimental seawater (2.22 nmol L^{-1}). Although statistically insignificant, mean chlorophyll-a for all Fe amended combinations at this site were enhanced relative to non-Fe treatments (control, +Co). This could suggest the substantial growth that occurred across all incubated bottles led to significant Fe drawdown, with the supplementary Fe supply enabling additional growth. However F_v/F_m in non-Fe treatments remained high, arguing against such an interpretation.

In contrast, Fe amendment—alone or in combination with Co or B₁₂—in experiments located further offshore (Experiments 2, 4 and 5), led to significant F_v/F_m increases relative to control and Co-amended bottles (Fig. 2). Significant increases in chlorophyll-a concentrations were also observed for all Fe-amended combinations in Experiments 2 and 4. In Experiment 5, although Fe stress was evident in the control and +Co bottles (i.e., having significantly lower F_v/F_m than Fe amended combinations), both F_v/F_m and chlorophyll-a declined from initial values, possibly caused by high levels of grazing and/or significant photoacclimation during

the incubation [e.g. *Behrenfeld and Milligan*, 2013]. Regardless of the latter, Experiments 2–5 collectively confirmed reductions in dissolved Fe in the transition offshore from the Peruvian coastline (Fig. 3a–b) as being a key driver for matching declines in chlorophyll-a (Fig 1a and Fig. 3c), and nighttime F_v/F_m (Fig. 3d), both measured in this study and previously under non-El Niño conditions by *Bruiland et al.* [2005].

3.3 Potential role for Co/vitamin B₁₂ in co-regulating phytoplankton yield in the Equatorial Pacific

Some limited evidence was found for Co and/or B₁₂ becoming serially limiting at the community level in the Peru upwelling following supply of Fe. For all experiments conducted in waters with elevated nitrate (Experiments 2–5), the mean chlorophyll-a response following amendment with Fe+Co or Fe+B₁₂ was always higher than that following amendment with Fe or Co alone (Fig. 2g–j). These responses were however not statistically resolvable, either within individual experiments (Fig. 2), or when normalized chlorophyll-a responses were aggregated across all experiments (not shown). Therefore, whilst mean changes at individual sites could be interpreted to suggest the potential for serial Co/B₁₂ limitation, such conditions were not fully established in these waters [cf. *Saito et al.*, 2005; *Bertrand et al.*, 2007; *Browning et al.*, 2017]. This may not have been the case if sites had been occupied further offshore (Fig. 4). Calculations using available GEOTRACES data show continued Co loss from surface waters, relative to Fe, with distance offshore from Peru. Eventually, the biological ‘excess’ of Co over Fe becomes less than SE Atlantic experimental sites where clear serial responses to Co addition have been observed previously [Fig. 4; *Resing et al.*, 2015; *Hawco et al.*, 2016; *Browning et al.*, 2017]. Acknowledging the potential for changes in community-level Co/B₁₂ demand and bioavailability, this enhanced loss of Co offshore from Peru could be hypothesized to result in similar observations of widespread serial or co-limitation by Co in the Equatorial Pacific [*Sañudo-Wilhelmy et al.*, 2012; *Bertrand et al.*, 2007, 2011, 2015; *Panzeca et al.*, 2008; *Helliwell et al.*, 2015, 2016; *Heal et al.*, 2017; *Saito et al.*, 2004, 2005].

3.4 Potential impact of El Niño conditions on chlorophyll-a

The isopycnal and macronutrient distribution in October 2015 suggested active wind-driven upwelling along the Peruvian shelf—despite El Niño status—but was dominated by warmer, more oxygenated waters than non-El Niño conditions [*Stramma et al.*, 2016]. Discrete sampling within the on-shelf, near coastal zone revealed high surface nitrate (13.6–23.6 $\mu\text{mol L}^{-1}$) and relatively high chlorophyll-a (up to 14.7 mg m^{-3} measured), as found during non-El Niño conditions [*Bruiland et al.*, 2005; *DiTullio et al.*, 2005].

Area-averaged, on-shelf satellite-derived chlorophyll-a for October 2015 was similar to a 2002–2016 climatology (Figs S1 and S4). However, there was a geographic redistribution of temporally averaged concentrations over the shelf, with positive anomalies (higher chlorophyll concentrations) in the near-coastal zone and negative anomalies (lower chlorophyll concentrations) further offshore towards the 1 km water depth contour (Fig. 1c, d). Geographically patchy, high magnitude chlorophyll-a anomalies in this region are common in the satellite record and not uniquely associated with El Niño events (Fig. S5). The one experiment conducted in the near-coastal zone (Experiment 3) led to chlorophyll-a accumulation in all incubated experimental bottles, including unamended controls (e.g., mean average of $3.5 \times$ chlorophyll-a increases in control bottles over initial concentrations). This suggested that these near-coastal seawaters, in addition to having sufficient macronutrients,

were also Fe/Co/B₁₂-replete, with experimental confinement potentially resulting in (i) relief of light limitation and/or (ii) isolation from grazing and/or (iii) prohibited dilution/dispersal, which subsequently allowed chlorophyll-a to accumulate [e.g., Moore *et al.*, 2006; Cullen *et al.*, 1992]. Given (micro)nutrient concentrations under non-El Niño conditions in this near-coastal regime are also elevated [Bruland *et al.*, 2005], such factors (i.e., enhanced light, reduced phytoplankton loss) could be hypothesized to have contributed to the positive satellite chlorophyll-a anomalies observed (Fig. 1c, d).

In contrast to near-coastal waters, experiments and across-shelf observations demonstrated a rapid offshore transition to Fe limited conditions (Experiments 2–5; Fig. 2). Changes in Fe supply offshore could therefore be an important factor regulating phytoplankton productivity in these waters [Bruland *et al.*, 2005; Johnson *et al.*, 1999], potentially resulting in the generally negative surface chlorophyll-a anomalies recorded by satellite away from the Peru coastline during our occupation (Fig. 3d). Although it is difficult to compare the surface-most (1–2 m depth) Fe concentrations presented here with those collected under non-El Niño conditions in the context of Fe delivery to the euphotic zone [Figure 3a,b; Bruland *et al.*, 2005], several factors can be hypothesized to have reduced bioavailable Fe supply under the atypical El Niño conditions characterizing our cruise occupation. Firstly, the upwelling of warmer, more oxygenated waters over the northern Peruvian shelf during our occupation may have reduced sedimentary Fe efflux and water column retention [Stramma *et al.*, 2016; Liu and Millero, 2002; Johnson *et al.*, 1999; Bruland *et al.*, 2005; Lohan and Bruland, 2008; Scholz *et al.*, 2016]. Secondly, warmer and more oxygenated seawaters may have reduced the solubility of inorganic Fe(III) species [Schlosser *et al.* 2012] and/or the fraction of dissolved Fe in the form of more bioavailable Fe(II) species [Liu and Millero, 2002; Shaked and Lis, 2012]. Thirdly, the formation and sinking of more biogenic particles in higher chlorophyll-a waters nearest the Peru coast would have removed more Fe from the dissolved pool, leaving less Fe to be advected offshore (Fig. 1d).

4. Conclusions

Following earlier studies testing for Fe limitation in the Equatorial Pacific [Martin *et al.*, 1994; Hutchins *et al.*, 2002; Eldridge *et al.*, 2004; Bruland *et al.*, 2005], five new bioassay experiments have confirmed a patchwork of community-level Fe limitation dictated by proximity to high-Fe coastal waters and position within the regional nitrate gradient. Our results suggest any reduction in offshore supply of bioavailable Fe could play a central role in reducing phytoplankton yields in proximity to the Peruvian shelf under El Niño conditions (Fig. 3; Barber and Chavez [1986]; Espinoza-Morriberón *et al.* [2017]). However, alongside Fe availability, the net effect of several environmental drivers affecting multiple trophic levels might be needed to resolve the mechanisms underpinning chlorophyll-a changes [Boyd *et al.*, 2014; Chen *et al.*, 2012; Behrenfeld and Boss, 2014; Mackas *et al.*, 1985; Ulloa *et al.*, 2001; Jackson *et al.*, 2011].

Evidence for Co and/or B₁₂ becoming serially limiting following Fe supply was confined to statistically insignificant mean chlorophyll-a enhancements following Fe+Co/B₁₂ addition relative to Fe alone. Alterations in Fe:Co supply ratios to surface waters, for example due to divergent metal source strengths (e.g., via modified aerosol or sediment supply), solubility controls (e.g., seawater oxidation state, temperature, ligand types/concentrations), and removal process (e.g., precipitation, scavenging, phytoplankton elemental stoichiometry), could regulate whether Co/B₁₂ (co-/serial)limitation ever occurs in the Peru upwelling [Saito *et al.*, 2004, 2005; King *et al.*, 2011; Koch *et al.*, 2011; Hawco *et al.*, 2016; Browning *et al.*,

2017]. Further offshore from the Peru coastline, open ocean GEOTRACES data shows continued Co loss relative to Fe in surface seawater, indicating that Co/B₁₂ co-/serial limitation could be at least as prevalent as that recently discovered in the SE Atlantic [Browning *et al.*, 2017], potentially playing a role in restricting phytoplankton growth and full nitrate drawdown following an excess supply of Fe [Martin *et al.*, 1994].

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Table 1. Starting conditions for bioassay experiments

	Experiment number				
	1 Eq. Pacific	2 Off-shelf Peru	3 On-shelf Peru	4 Off-shelf Peru	5 Mid-shelf Peru
Longitude (°W)	85.49	82.42	78.50	77.94	75.89
Latitude (°N)	0.82	-8.34	-9.97	-13.10	-15.67
Coast distance (km)	420	266	26	143	73
SST (°C)	26.2	22.3	17.8	18.2	18.0
SST variability (°C) [†]	3.2	2.4	3.2	2.9	4.1
MLD (m)	21.0	~20 [‡]	~13 [‡]	33.8	24.5
NO ₂ +NO ₃ (μmol L ⁻¹)	0.06	7.46	20.33	26.02	9.67
PO ₄ (μmol L ⁻¹)	0.20	1.02	1.79	2.18	1.31
SiO ₂ (μmol L ⁻¹)	1.09	3.34	14.14	16.13	6.15
dFe (nmol L ⁻¹)	0.06	0.13	2.22	0.31	0.68
dCo (nmol L ⁻¹)	0.021	0.041	0.086	0.13	0.11
Fe _N * (nmol L ⁻¹)	0.036	-2.86	-5.93	-10.12	-3.20
Co _{Fe} * (nmol L ⁻¹)	0.019	0.038	0.030	0.122	0.093
Chl-a (mg m ⁻³)	0.20	0.33	4.26	1.45	1.62
F _v /F _m	0.30	0.31	0.47	0.37	0.44
Dominant accessory pigments	Zea> 19'Hex> 19'But	Fuco> 19'Hex> Chl c1+c2	Fuco> Chl-b> Chl c1+c2	19'Hex> Chl-b> 19'But	Chl-b> 19'But> 19'Hex
Dominant phytoplankton	Cyanobacteria, Haptophytes	Diatoms, Haptophytes,	Diatoms, Chlorophytes	Haptophytes, Chlorophytes	Chlorophyte, Haptophytes

Fe_N* and Co_{Fe}* are Fe and Co concentrations in excess of assumed-average phytoplankton requirements relative to nitrate and Fe respectively:

$$\text{Fe}_N^* = \text{Fe} - (\text{NO}_2 + \text{NO}_3) R_{\text{Fe:N}}$$

$$\text{Co}_{\text{Fe}}^* = \text{Co} - \text{Fe} R_{\text{Co:Fe}}$$

Where $R_{\text{Fe:N}}$ and $R_{\text{Co:Fe}}$ are assumed-average Fe:N (0.469×10^{-3} mol:mol) and Co:Fe (0.025 mol:mol) stoichiometry in phytoplankton [Moore *et al.*, 2013]. After Parekh *et al.* [2005] and Ito *et al.* [2005].

Zea=Zeaxanthin; 19'Hex=19'-Hexanoyloxyfucoxanthin; 19'But= 19'-butanoyloxyfucoxanthin;

Fuco=Fucoxanthin

[†]Maximum variability in underway SST over the time course of the incubation

[‡]Calculated from nearest CTD station profile

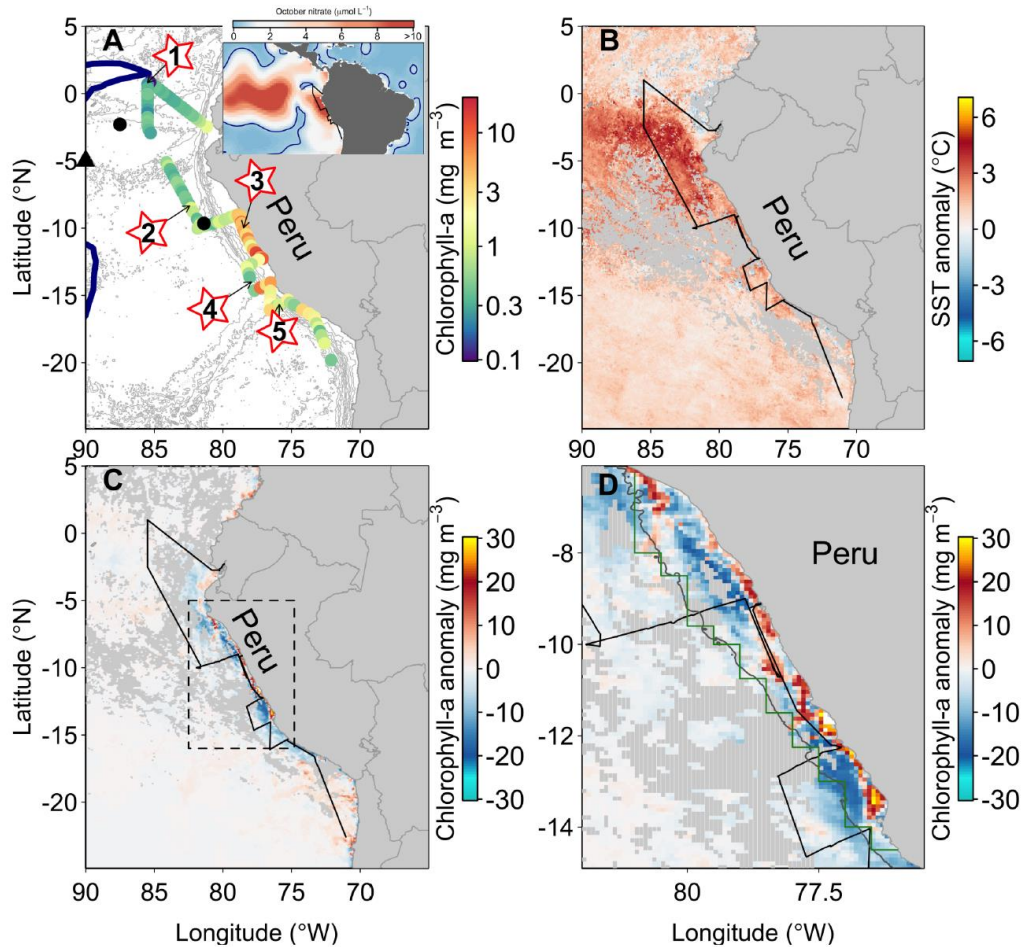


Figure 1. Study region highlighting the biogeochemical setting during occupation. (a) Cruise track showing measured chlorophyll-a concentrations (colored dots) and incubation experiment locations (numbered stars). Grey contours show bathymetry (1 km depth intervals). Black dots and triangle respectively show the locations of bottle-scale Fe amendment experiments performed by *Hutchins et al.* [2002] and IronExI reported by *Martin et al.* [1994]. The blue line is the $0.5 \mu\text{mol L}^{-1}$ climatological World Ocean Atlas (WOA) nitrate contour for October, displayed for a wider region in the inset map. (b) October 2015 SST anomaly (October 2015 data subtracted from 2002–2016 October climatology). (c) As for ‘b’ but for chlorophyll-a concentration. (d) Boxed region in ‘c’ highlighting Peruvian shelf chlorophyll-a anomalies. Dark grey line is the 1 km depth contour and green line highlights the region used for calculating shelf-averaged chlorophyll-a anomalies (Figs S1 and S4).

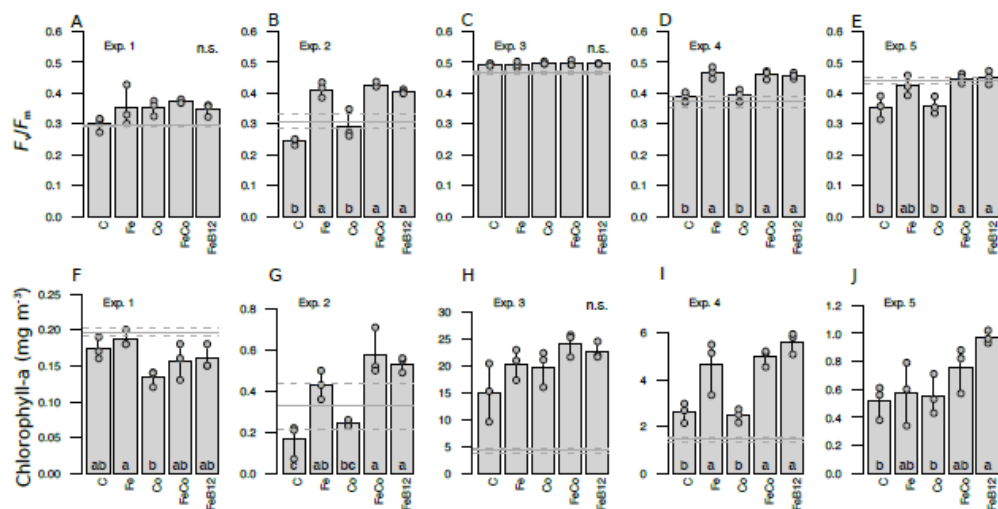


Figure 2. Phytoplankton responses to nutrient amendment. (a–e) F_v/F_m and (f–j) chlorophyll-a biomass changes bioassay experiments. Bar heights indicate means ($n=3$); dots show individual bottle replicates and lines indicate the range ($n=3$). Letters show the results of a test for statistically significant different means (ANOVA $p < 0.05$ followed by a Tukey Honesty Significant Difference test): bars labeled with the same letter are statistically indistinguishable and n.s.= not significant. Grey horizontal lines indicate initial conditions (dashed lines=range; solid lines=mean). The mean starting chlorophyll-a in Experiment 5 was 1.62 mg m^{-3} .

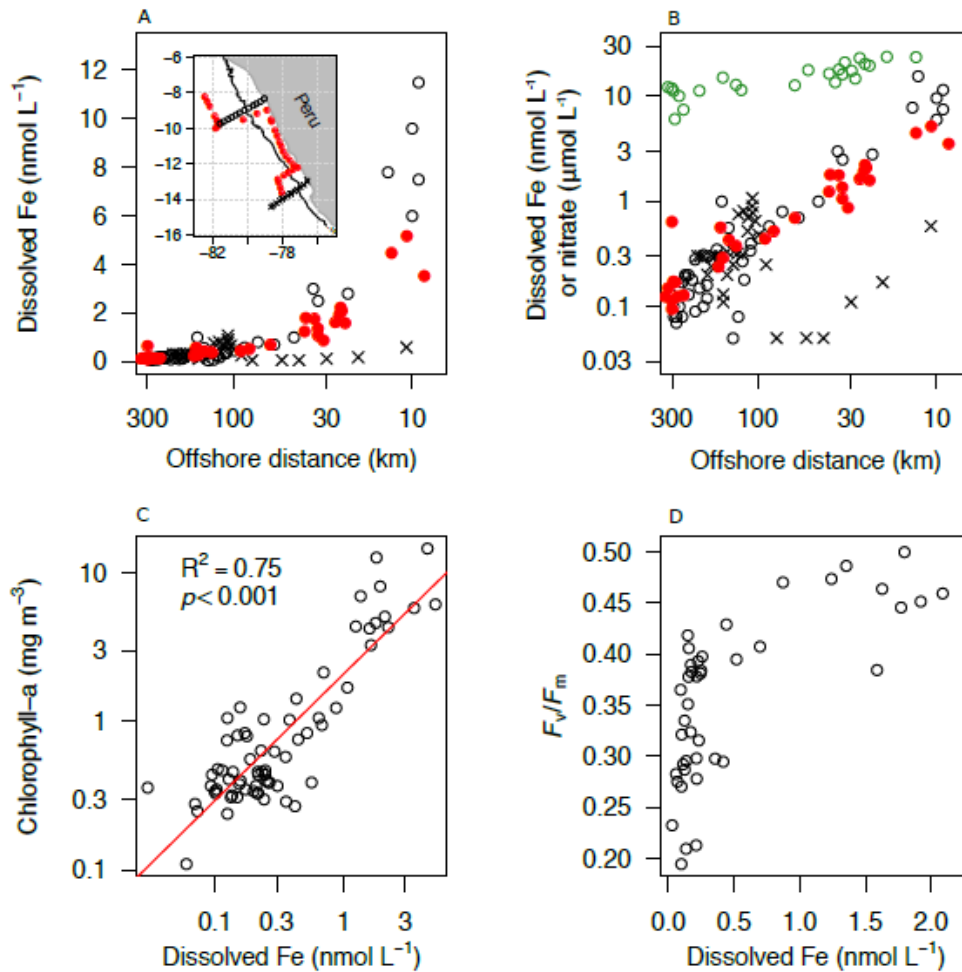


Figure 3. Potential impact of Fe availability on phytoplankton. (a) Offshore decline in surface dissolved Fe concentrations (note logarithmic distance scaling). Red dots are data from this study (locations highlighted in inset map) and black symbols are data from *Bruland et al.* [2004] (from *Tagliabue et al.* [2012] dataset) for two transects that ran perpendicular to the coast. Shelf width is highlighted by the 1 km depth contour on the inset map. The southern cross-shelf transect of *Bruland et al.* [2004] had lower Fe concentrations (crosses) than more northerly transects in both studies, probably resulting from a narrower shelf width for sedimentary Fe entrainment into upwelled waters [*Bruland et al.*, 2004]. (b) Same as ‘a’ but with dissolved Fe on a logarithmic scale. Surface nitrate concentrations from this study (same sampling locations as ‘a’) are plotted in green. (c) Correlation of log-transformed dissolved Fe and chlorophyll-a biomass (note for linear correlation: $R^2 = 0.67$, $p < 0.001$). (d) Dissolved Fe and F_v/F_m .

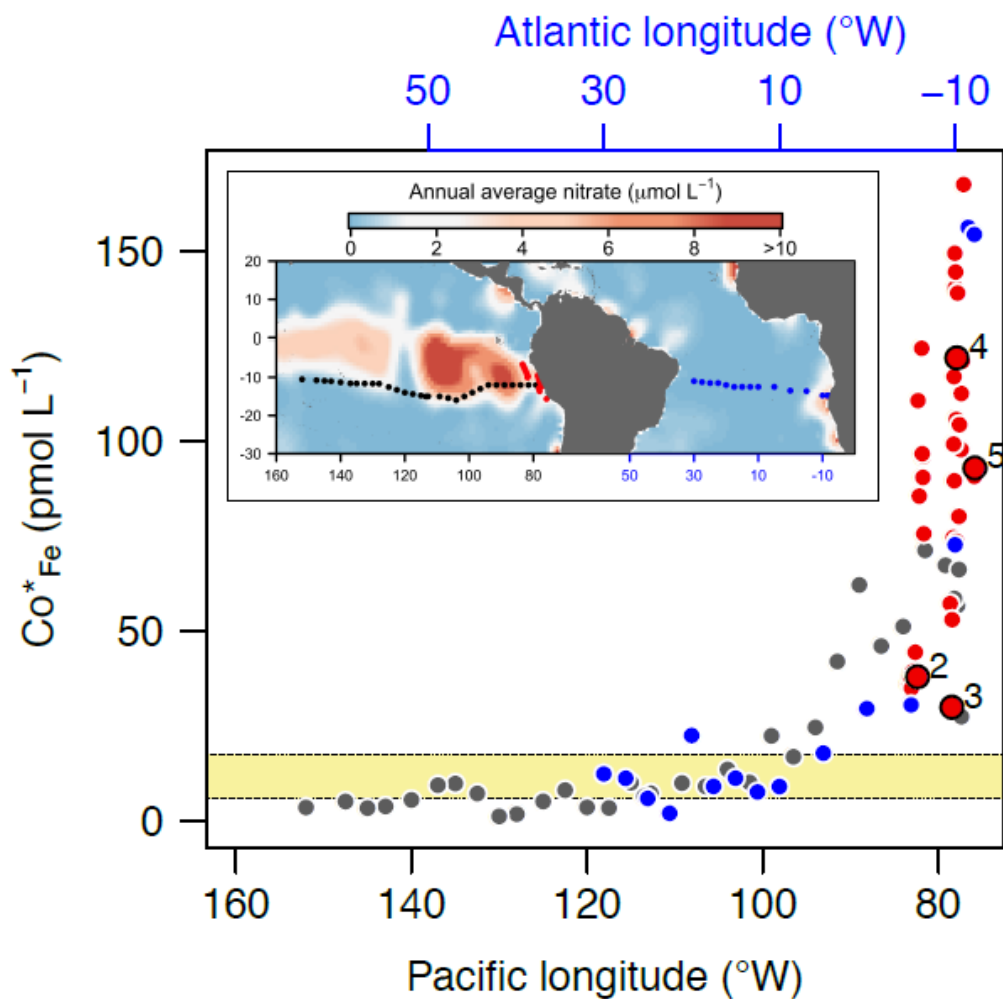


Figure 4. Potential for Co serial/co-limitation offshore of the Peru upwelling. Vertical axis is Co_{Fe}^* , the ‘excess’ dissolved Co concentration relative to Fe assuming average phytoplankton requirements (see Table 1). Red dots indicate Co_{Fe}^* for the Peru upwelling region (this study), with initial values for the four bottle incubation experiments in this zone labeled. The black and blue data points represent surface waters (<10 m depth) of the GEOTRACES GP16 and GAc01 cruises respectively [Resing *et al.*, 2015; Hawco *et al.*, 2016; Noble *et al.*, 2012]. Yellow shading highlights the Co_{Fe}^* range at experimental sites exhibiting significant serial Co limitation in the SE Atlantic [Browning *et al.*, 2017]. Note the Atlantic-Pacific cruises were at similar latitudes, and that the two ocean basins represented in the figure have longitude scales that differ but are of the same absolute magnitude.