Depletion of micronutrient trace metals in Line P surface waters during the 2014 warming anomaly: Implications for marine ecosystems and climate change

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2018 PICES Annual Meeting, Yokohama, Japan
NE Pacific Warming Anomaly

• After seven years of mainly cool conditions, surface waters in the NE Pacific began to warm in 2013, the most extreme warming arriving in early 2014 in the mid-Gulf of Alaska.

• This feature, nicknamed “The Blob”, was the warmest temperature anomaly ever observed in the region, reaching more than 3°C above normal.

• Stratification due to formation of the anomaly inhibited seasonal mixing along Line P, fundamentally altering conditions in the surface waters along this transect.
Temperature along Line P

August 2012  August 2014  June 2016

BEFORE  DURING  AFTER

- Line P cruises take place in Winter (February), Spring (May/June) and Summer (August/September).
- Data collected on every cruise include depth profiles of temperature, salinity, $\sigma_T$ (density) and dissolved oxygen, as well as chlorophyll and major nutrients.
The Line P Iron Time Series

• Fe measurements have been made along Line P since 1997, providing a unique time series of such measurements between the iron-rich coastal waters of British Columbia and HNLC waters of the Alaska gyre.

• this Iron Time Series can help us to ‘benchmark’ Fe concentrations along Line P, study processes by which Fe is introduced to the open ocean, and evaluate the potential impacts of natural and anthropogenic Fe inputs.
The Line P Iron Program

• In 2012 Fisheries and Oceans Canada scientists together with collaborators at the universities of Victoria, Laval and British Columbia established the Line P Iron Program to ensure the continuity of iron measurements along Line P and provide a framework for process studies of Fe and other trace elements in the NE Pacific.

• goals include investigating how the distribution and speciation of Fe, Cu and other trace elements affect, and are influenced by, processes such as hypoxia, stratification, ocean acidification and climate change.
Research Timeline at Ocean Station Papa

OCS Station Papa Mooring

NSF Carbon Cycle Process Study
ADCP mooring: Near-Inertial Wave Propagation into Deep Ocean Study
Wave Mooring: NSF Impact of Waves on Ocean Mixed Layer Study

Canadian DFO P-Line Program

HISTORICAL LINE-P IRON DATASET
LINE-P IRON PROGRAM DATA
Iron Sampling Along Line-P

Op = optional if time and conditions allow
✓ ✓ = 2 Filtered and 2 Unfiltered samples
✓ = 1 Filtered and 1 Unfiltered sample

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Sampling for Iron and other Trace Metals

- Samples are collected using acid-washed Niskin or Go-Flo bottles mounted on a Kevlar line and/or Trace Metal Rosette, filtered (0.2-µm), acidified (pH 1.7) and stored according to GEOTRACES protocols.

*Trace Metal Sampling on Line-P*
*(Photos: Christina Schallenberg)*
Variation in Dissolved Trace Metals during the 2014 Warming Anomaly

• To capture the impact of the “Blob” on the availability of biologically important trace metals (micronutrients) to marine phytoplankton we measured the concentrations of these metals in seawater samples collected between 2012 and 2016 as part of the Line P Iron Program.
Micronutrient Trace Metals

- **Nickel (Ni):** co-factor in urease, an enzyme involved in the assimilation of urea by marine phytoplankton, which can be co-limited by Ni and urea in surface waters.

- **Zinc (Zn):** co-factor in carbonic anhydrase (CA), an enzyme involved in photosynthesis, and may limit or co-limit primary productivity in the open ocean.

- **Cadmium (Cd):** known to substitute for Zn as the co-factor in CA, and may exert controls on community composition and productivity.

- **Cobalt (Co):** co-factor in vitamin B\textsubscript{12}; can substitute for Zn in diatoms and is required by certain cyanobacteria and coccolithophores.

- **Iron (Fe):** plays an essential role in phytoplankton metabolism, including photosynthesis and nitrogen fixation, and limits primary productivity in up to 50% of the surface ocean.

- **Copper (Cu):** can be toxic at elevated concentrations but is an important micronutrient in low-Fe waters, where Cu-containing enzymes can replace Fe-containing analogues.
Analysis of Trace Metals

- Trace metals were pre-concentrated on an ESI seaFAST system and analysed using an Agilent 8800 triple quadrupole ICP-MS/MS instrument at UVictoria.
• CTD measurements show surface waters to be warmer and less dense in 2014 than in 2012 or 2016.
P26: Major Nutrients

- CTD measurements show surface waters to be warmer and less dense in 2014 than in 2012 or 2016.

- Bottle measurements also show a decrease in Major Nutrients during (and for Silicate, after) the “Blob”.
Dissolved Ni, Co and Cd also showed significant depletion in surface waters in 2014, during the “Blob”. These micronutrient trace metals act as, or can substitute for, co-factors in key enzymes.
P26: Ni, Co and Cd

- By June 2016 these micronutrients had almost returned to August 2012 (pre-“Blob”) levels at P26.
• By June 2016 these micronutrients had almost returned to August 2012 (pre-“Blob”) levels at P26.
• However, they stayed relatively low at P20, consistent with shoreward movement of the “Blob”.
P20: Major Nutrients

- Bottle measurements show particular depletion of major nutrients at stations P20 and P16 in the transition zone between open ocean and continental shelf.
*Bottle measurements show particular depletion of major nutrients at stations P20 and P16 in the transition zone.*

**P16: Major Nutrients**

- **Temp (°C)**
- **Sigma-t (mg/m³)**
- **Chl-a (µmol/L)**
- **Nitrate (µmol/L)**
- **Phosphate (µmol/L)**
- **Silicate (µmol/L)**
Bottle measurements show particular depletion of major nutrients at stations P20 and P16 in the transition zone.

This is consistent with increased stratification, which inhibits the vertical mixing of nutrient-rich deep water to the surface.
Higher surface chlorophyll in June 2016 (post-“Blob”) is consistent with a breakdown in stratification.
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• However, Major Nutrients and Cd remained depleted at the transition stations P20 and P16.
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However, Major Nutrients and Cd remained depleted at the transition stations P20 and P16.
Variation in Nitrate (mmol/m$^3$)

- the summer nitrate minimum zone extended much further offshore (beyond station P20) during 2014 (Pena et al., 2018) but was returning to pre-“Blob” conditions by 2016.
Variation in Silicate (mmol/m$^3$)

- In contrast, summer silicate levels remained relatively low between P20 and P26 in 2016 (Pena et al., 2018).
Phytoplankton Responses

P26 (HNLC region)

• Phytoplankton biomass was unusually high in the summer of 2014 (during the “Blob”).
• Phytoplankton composition in 2016 similar to that in 2013 (pre-“Blob”) except for increase in diatoms, but biomass again unusually high in the spring of 2016 (post-”Blob”).

P20 and P16 (low Nitrate region)

• Unusually low phytoplankton biomass and a dramatic increase in cyanobacteria in 2014.
• Surface nutrients and phytoplankton biomass in 2016 still remained relatively low.
Line P Phytoplankton Community

Summer 2013

Summer 2014

Summer 2016

[Pena et al., 2018]
(Micro)Nutrient Responses

P26
• Ni, Co and Cd significantly depleted in surface waters in 2014 (along with Nitrate and Phosphate) but return to near normal in 2016 (whereas Silicate remains depleted).

P20
• Ni, Co and Cd depleted to slightly great depth than at P26 in 2014 and remain low (esp. Cd) in 2016 (along with Nitrate, Phosphate and, in particular, Silicate).

P16
• Ni, Co and Cd depleted to a slightly greater depth than at P20 in 2014 but return to near-normal in 2016 (Nitrate, Phosphate and, particularly, Silicate remain low).
Co-limitation by micronutrients?

P26
- Apparent drawdown of micronutrient trace metals in 2014 consistent with increase in phytoplankton biomass.
- Low Silicate in 2016 consistent with an increase in diatoms in HNLC waters.

P16 and P20
- Low biomass from 2014 to 2016 consistent with (micro)nutrient limitation.
- Dramatic increase in cyanobacteria at P20 in 2014 may be linked to apparent drawdown of Co.

Almost complete depletion of Cd in 2014 and 2016 suggest that it may be co-limiting phytoplankton growth.
Response at Station P26

- Chl measurements at P26 in summer 2014 and spring 2016 were unusually high [Pena et al., 2018].
- Previous studies have shown that phytoplankton growth is co-limited by light and iron in the subarctic NE Pacific.
- Meso-scale Fe addition experiments in the Alaska Gyre have shown that adding Fe to the upper mixed layer increases the abundance of microplanktonic diatoms [PICES Scientific Report No. 31, 2006].
- Evolution of temperature anomalies from an NPGO-like pattern in 2014 to a PDO-like pattern in 2015 resulted in persistence of the warm anomaly [Di Lorenzo and Mantua, 2016].
P26: Dissolved Fe

- Data from the Line P Iron Program shows that Fe in surface water at P26 during the summer was low before and during the “Blob”.
- Data from the Line P Iron Program showed that Fe in P26 surface waters during the summer was low before and during the “Blob”.

- However, dissolved Fe measured in June 2016 was higher than seen in February 2014 (which is expected to be higher due to minimal drawdown of Fe in winter).
• Seasonal and inter-annual variability in dFe between 2012 and 2016 were greater than seen historically between 1997 and 2011, except during 1999 and 2005.

• In each case, cooling after a significant warming event (i.e. “Blob” or El Niño) was accompanied by higher dFe.
Dissolved Cu was also elevated in June 2016, although Cu and Fe were lower in surface waters in August 2014.
Sources of Fe?

• Changing circulation patterns associated with ENSO/NPGO/PDO may result in the advection of Fe from iron-rich coastal waters to offshore Line P stations (e.g. via mesoscale eddies) during or following warming events.

• Increased stratification associated with warming may promote remineralization of organic matter just below the mixed layer, resulting in the release of Fe (and other organically complexed metals like Cu) that can mix into surface waters when stratification begins to break down.

• Research to further investigate these processes, and identify components of marine dissolved organic matter (ligands) that bind and regulate uptake of micronutrients like Fe and Cu [Nixon and Ross, 2016], is under way.
Conclusions

1) Similar trends in major and micronutrients indicate that both became less available in surface waters during the “Blob” and that changes in phytoplankton ecology attributed to the former (Pena et al., 2018) may also have been affected by drawdown of trace metals.

2) Unusually high Chl at Station P in 2016, following the “Blob”, may be associated with higher then normal Fe concentrations resulting from changes in ocean circulation or vertical mixing of (micro)nutrients released by remineralization of organic matter during stratification.

3) The impact of stratification, and the resulting availability of (micro)nutrients, on phytoplankton biomass and species composition (incl. smaller/slow sinking species) has implications for carbon export and climate change.
PICES 2019

• Taking place in Victoria BC, Canada

• Proposed Session:
  “Linking changes in climate, (micro)nutrient distribution, phytoplankton ecology, and production of algal exudates in the North Pacific”.

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THANK-YOU!