

## Volcanic ash fuels anomalous plankton bloom in subarctic northeast Pacific

Roberta C. Hamme,<sup>1</sup> Peter W. Webley,<sup>2</sup> William R. Crawford,<sup>3</sup> Frank A. Whitney,<sup>3</sup> Michael D. DeGrandpre,<sup>4</sup> Steven R. Emerson,<sup>5</sup> Charles C. Eriksen,<sup>5</sup> Karina E. Giesbrecht,<sup>1</sup> Jim F. R. Gower,<sup>3</sup> Maria T. Kavanaugh,<sup>6</sup> M. Angelica Peña,<sup>3</sup> Christopher L. Sabine,<sup>7</sup> Sonia D. Batten,<sup>8</sup> Laurence A. Coogan,<sup>1</sup> Damian S. Grundle,<sup>1</sup> and Deirdre Lockwood<sup>5</sup>

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[1] Using multiple lines of evidence, we demonstrate that volcanic ash deposition in August 2008 initiated one of the largest phytoplankton blooms observed in the subarctic North Pacific. Unusually widespread transport from a volcanic eruption in the Aleutian Islands, Alaska deposited ash over much of the subarctic NE Pacific, followed by large increases in satellite chlorophyll. Surface ocean pCO<sub>2</sub>, pH, and fluorescence reveal that the bloom started a few days after ashfall. Ship-based measurements showed increased dominance by diatoms. This evidence points toward fertilization of this normally iron-limited region by ash, a relatively new mechanism proposed for iron supply to the ocean. The observations do not support other possible mechanisms. Extrapolation of the pCO<sub>2</sub> data to the area of the bloom suggests a modest ~0.01 Pg carbon export from this event, implying that even large-scale iron fertilization at an optimum time of year is not very efficient at sequestering atmospheric CO<sub>2</sub>. **Citation:** Hamme, R. C., et al. (2010), Volcanic ash fuels anomalous plankton bloom in subarctic northeast Pacific, *Geophys. Res. Lett.*, 37, L19604, doi:10.1029/2010GL044629.

### 1. Introduction

[2] Ocean production and export of organic carbon transfers CO<sub>2</sub> from the atmosphere to the ocean interior. In ~20% of the ocean, productivity is limited by low iron concentrations despite plentiful nutrients like nitrate. The subarctic NE Pacific is one of these high nutrient/low chlorophyll (HNLC) regions [Harrison *et al.*, 2004], where

purposeful additions of iron have been shown to increase productivity [Boyd *et al.*, 2004; de Baar *et al.*, 2005]. Over 50 years of observations at Station P (50°N 145°W, Figure 1f) have demonstrated low productivity in this region, punctuated by occasional blooms attributed to iron input [Peña and Varela, 2007; Whitney and Freeland, 1999; Boyd *et al.*, 1998].

[3] Natural iron fertilization of HNLC regions by atmospheric deposition of dust may occur [Fung *et al.*, 2000; Gabric *et al.*, 2010] and has been proposed to play a role in reducing atmospheric CO<sub>2</sub> during ice ages, though this is controversial [Martin, 1990; de Baar *et al.*, 2005]. Purposeful fertilization of these areas with iron to reduce atmospheric CO<sub>2</sub> levels has been explored for climate mitigation, but the potential impact is speculative and may involve negative ecological consequences. Recently, atmospheric deposition of volcanic ash has been proposed as an intermittent source of iron to the sea, potentially explaining some features in the atmospheric CO<sub>2</sub> record [Watson, 1997; Duggen *et al.*, 2007, 2010]. In this paper, we show compelling evidence that volcanic ash does stimulate blooms in HNLC regions, but that the impact on atmospheric CO<sub>2</sub> is not necessarily significant.

### 2. Methods

[4] Field and laboratory methods are outlined in the auxiliary material.<sup>1</sup>

### 3. Evidence for Iron Fertilization by Volcanic Ash

[5] In August 2008, the subarctic NE Pacific experienced the largest phytoplankton bloom observed in the 12-years of chlorophyll records from SeaWiFS and MODIS ocean color satellites (Figure 1). The area of enhanced surface chlorophyll covered the eastern iron-limited region [Langmann *et al.*, 2010a]. Monthly-mean chlorophyll averaged over 48–56°N, 136–150°W (8.5\*10<sup>5</sup> km<sup>2</sup>) was twice as high (0.9–1.3 mg m<sup>-3</sup>) as any previous month dating to September 1997 (Figure 1e).

[6] The spatial extent of the subarctic NE Pacific bloom visually matches the dispersal, and likely deposition, of volcanic ash from the 7–8 August 2008 eruption of Kasatochi volcano (52.2°N 175.5°W) in the Aleutian Islands, Alaska, USA. This eruption injected airborne ash into a

<sup>1</sup>School of Earth and Ocean Sciences, University of Victoria, Victoria, British Columbia, Canada.

<sup>2</sup>Geophysical Institute, Alaska Volcano Observatory, University of Alaska Fairbanks, Fairbanks, Alaska, USA.

<sup>3</sup>Institute of Ocean Sciences, Fisheries and Oceans Canada, Sidney, British Columbia, Canada.

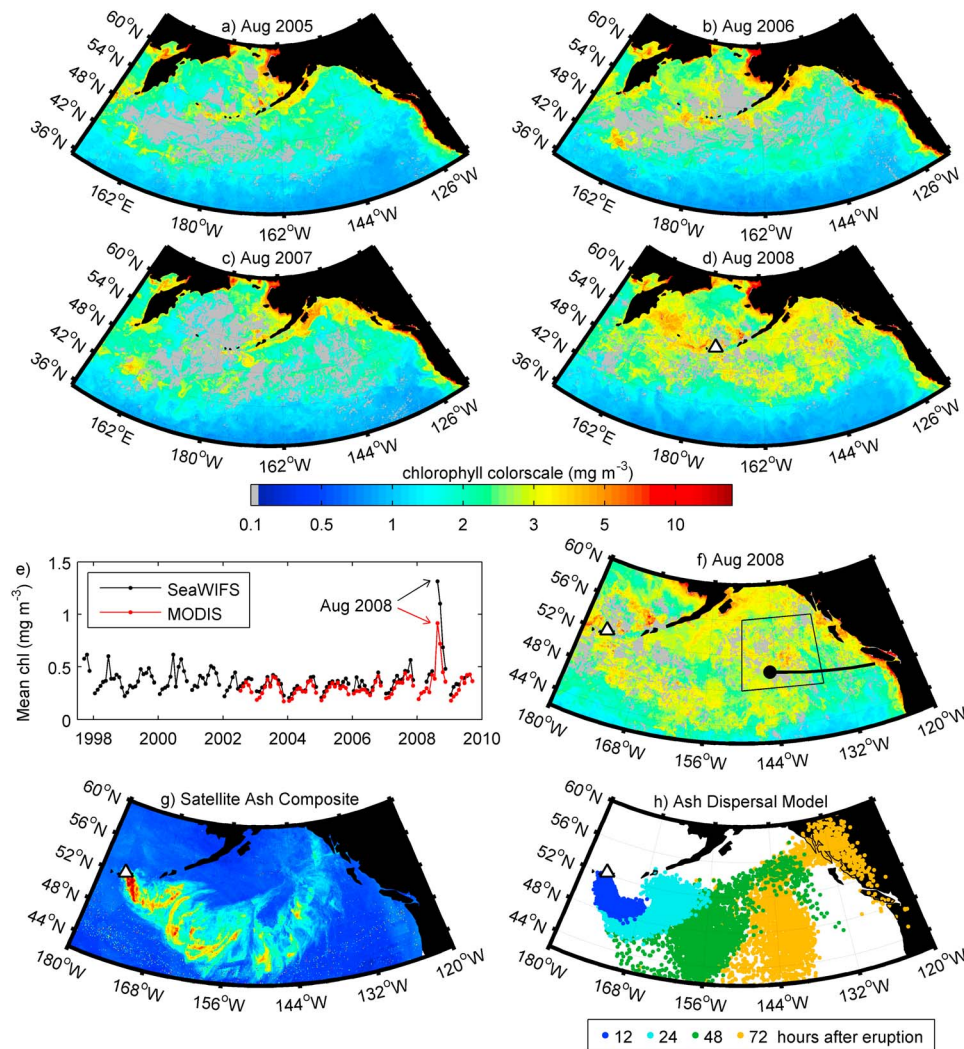
<sup>4</sup>Department of Chemistry and Biochemistry, University of Montana, Missoula, Montana, USA.

<sup>5</sup>School of Oceanography, University of Washington, Seattle, Washington, USA.

<sup>6</sup>College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, Oregon, USA.

<sup>7</sup>Pacific Marine Environmental Laboratory, National Oceanic and Atmospheric Administration, Seattle, Washington, USA.

<sup>8</sup>Sir Alister Hardy Foundation for Ocean Science, Plymouth, UK.

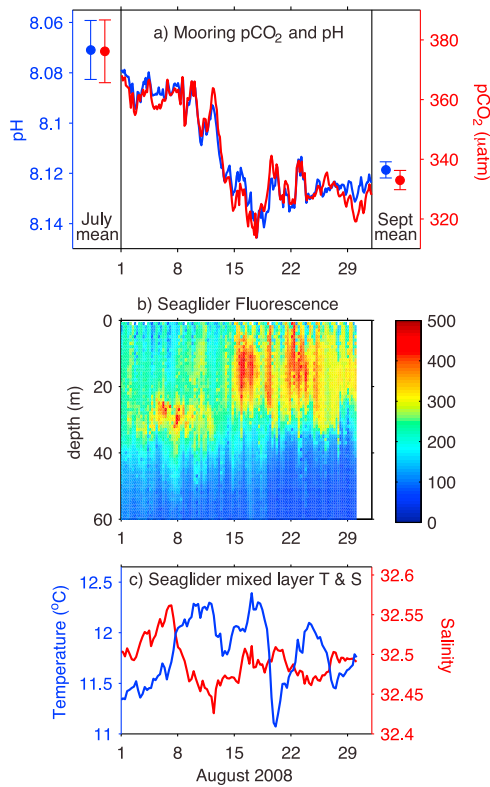


**Figure 1.** (a–d) North Pacific MODIS monthly-averaged surface chlorophyll in August 2005, 2006, 2007, 2008. (e) Time-series of monthly mean chlorophyll averaged over box shown in Figure 1f. (f) Zoom on subarctic NE Pacific MODIS August 2008 chlorophyll, same spatial grid as Figures 1g and 1h. Box shows area of time series averaging. Line from coast shows mid-August cruise track. Point at end of line shows Station P. White triangles show Kasatochi volcano. (g) Composite of most intense satellite detections of airborne ash from the Kasatochi eruption. (h) Particle locations at 0–10,000 m altitude from ash dispersal model at 12, 24, 48, and 72 hours after the start of the Kasatochi eruption.

forming storm that subsequently swept across the subarctic NE Pacific. Airborne ash was detected from the brightness temperature difference between 10–11  $\mu\text{m}$  and 11–12  $\mu\text{m}$  thermal radiation satellite data. A negative difference, indicates dry, fine-grained ash of radius 1–12  $\mu\text{m}$ . This technique shows transport over a wide area southeast of the volcano (Figure 1g). As ash became coated with water in the storm, it could not be detected by this method, compromising satellite detection to the northeast. Lagrangian modeling of ash dispersal, based on a theoretical distribution of particles from the eruption moving in prevailing winds derived from a weather prediction model, suggests transport and dry deposition farther to the east and north, covering the region of the bloom (Figure 1h). Another modeling study indicated that both wet deposition and gravitational settling caused ash fallout that covered the area of the bloom [Langmann *et al.*, 2010b]. Laboratory experiments in which fresh volcanic ash was added to seawater show large iron

releases within hours, likely from surface-adsorbed metal complexes, and stimulation of diatom growth in incubation experiments [Duggen *et al.*, 2007; Jones and Gislason, 2008]. Therefore, this eruption's ash would have immediately released some bioavailable iron to the ocean surface upon deposition.

[7] Scanning Electron Microscopy (SEM) combined with Energy Dispersive Spectroscopy of particles obtained from a single archived sample from 20-m depth at Station P on 21 August 2008 revealed 1–3 non-biological particles per 25 mL. These 10–20  $\mu\text{m}$  particles had shapes and elemental compositions typical of intermediate composition volcanic ash, dominated by Si, with abundant Al, Mg, Fe and Ca, and minor Na, K and Ti. Their compositions were not consistent with most airborne dust minerals, except possibly amphibole, anecdotally supporting possible ashfall at this location.

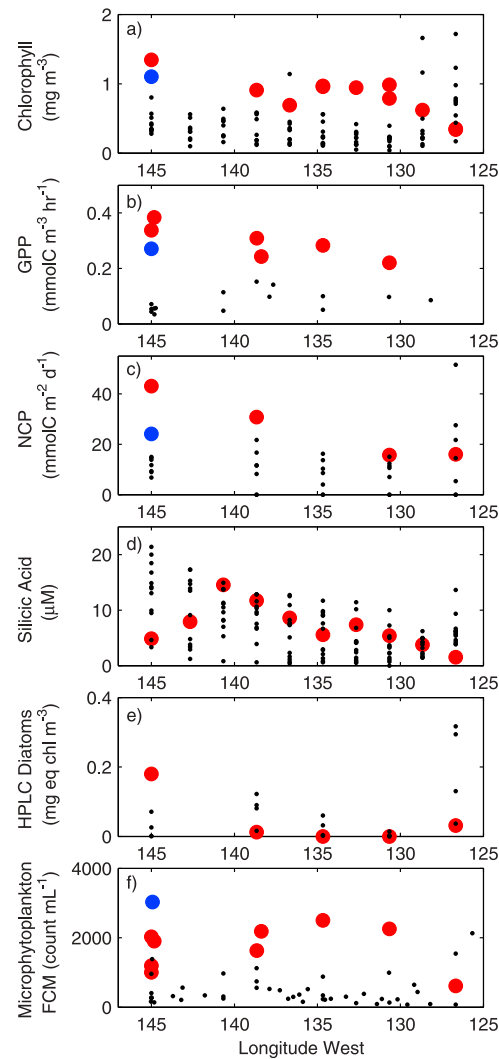


**Figure 2.** (a) Aqueous pCO<sub>2</sub> (red) and pH (blue) measured at the surface from a mooring at Station P. pH scale is reversed. Means and standard deviations for July and September 2008 shown. (b) Raw chlorophyll fluorescence signal measured by a Seaglider within 35 km of Station P. (c) Seaglider temperature and salinity averaged over upper 20 m.

[8] Observations from autonomous instruments establish the timing of the bloom event. Beginning 13 August 2008, surface water pCO<sub>2</sub>, measured on a mooring at Station P, began decreasing while surface pH, from the same mooring, began increasing, after both had been stable through July and early August (Figure 2a). These changes could only have been caused by organic carbon production (S. R. Emerson et al., Production rates of CaCO<sub>3</sub> and organic carbon in ocean surface waters from in situ measurements of pCO<sub>2</sub> and pH, submitted to *Global Biogeochemical Cycles*, 2010). Beginning 15 August, a Seaglider collecting profiles within a 50 × 50-km box centered on the mooring recorded high fluorescence in the surface mixed layer, lasting at least two weeks (Figure 2b), but only minor changes in temperature and salinity (Figure 2c). High fluorescence over the wider area, without temperature/salinity variations, indicates that changes in pCO<sub>2</sub> and pH were caused by productivity, not advection of an anomalous water mass. These observations mark the start of the bloom event and support the volcanic ash iron-fertilization hypothesis. The dispersal model predicts ash arrival from the Kasatochi eruption at Station P on 11 August 2008. An in situ, iron-fertilization experiment (SERIES) performed at Station P in July 2002 observed a four-day lag from iron addition to increased surface chlorophyll and clearly lower pCO<sub>2</sub> [Boyd et al., 2004; Wong et al., 2006]. Changes in pCO<sub>2</sub> and pH (indicating active growth) for two to five days following ash

deposition and increasing surface fluorescence (indicating biomass accumulation) by day four are consistent with the timing of the SERIES results.

[9] Measurements from two oceanographic cruises in late August 2008 confirm high chlorophyll and productivity rates. Discrete surface chlorophyll west of 130°W was twice the normal late summer concentration, confirming satellite observations (Figure 3a). Gross primary production (GPP) (Figure 3b), from surface short-term <sup>14</sup>C incubations, on both August 2008 cruises was twice that observed on previous spring and summer 2007–2008 cruises. Net community production (NCP) (Figure 3c), from mixed-layer O<sub>2</sub>/Ar mass balances that integrate over 6–10 days, was nearly double other spring and summer measurements at 145°W



**Figure 3.** Red circles show measurements along a cruise transect from 15 August (coastal at 125°W) to 21 August 2008 (Station P at 145°W). Blue circles show measurements at Station P on 31 August. Black dots show measurements from other years. For (a) chlorophyll and (d) silicic acid, black dots show Aug or Sep measurements in 1988–2004 [Peña and Varela, 2007]. For (b) GPP and (f) FCM data, black dots show June and August 2007, and June 2008. For (c) NCP, black dots show June and August 2007–2009, excepting August 2008. For (e) HPLC data, black dots show September 2006, June and August 2007, and June 2008.

(Station P) and also higher at 138°W. NCP measured at Station P ten days later had fallen, but was still higher than previous measurements. Near 145°W, surface silicic acid (Figure 3d) and nitrate concentrations in mid-August 2008 were lower than average values in previous years, suggesting biological drawdown.

[10] As expected, the more integrative measurements (NCP and nutrients) show a greater response to the west on this transect. Ash deposition occurred over the region on 11–12 August. The transect cruise began sampling at the coast (127°W) on 15 August and reached Station P (145°W) on 21 August, so the western stations were sampled later in the bloom. The SERIES experiment did not observe nutrient decreases until 11 days after iron enrichment [Boyd *et al.*, 2004], which matches our observations of lower nutrients only at the western-most stations. Surface ammonium concentrations and oxidation rates at Station P on 21 August 2008 were three or more times higher than on three 2009 cruises, indicative of nutrient recycling and at least mid-bloom conditions at that time.

[11] Community structure measurements showing diatom growth further support iron-fertilization. HPLC-determined surface pigment concentrations indicative of diatoms (Figure 3e), primarily fucoxanthin, were higher at 145°W (Station P) in August 2008 than previously observed along this transect except near the coast. Flow cytometry (Figure 3f) indicated higher numbers of large microphytoplankton (including diatoms) in surface waters west of 130°W in late August 2008. Both methods indicate that diatoms and other large cells were abundant on the western end of the transect. Also, a silicic acid-to-nitrate uptake ratio greater than 2 was observed at Station P in August 2008, demonstrating strong utilization by diatoms [Whitney *et al.*, 2005]. Iron-enrichment experiments, including SERIES, observe large increases in diatom abundances that come to dominate the phytoplankton community [Boyd *et al.*, 2004; de Baar *et al.*, 2005]. The presence of increased diatom numbers and silicic acid drawdown in late August 2008 shows that the region experienced iron input to the surface waters.

#### 4. Evidence Against Other Hypotheses

[12] High chlorophyll and low silicic acid events in this region have been attributed to natural iron enrichments [Whitney *et al.*, 2005] through transport from the coast by mesoscale eddies [Crawford *et al.*, 2007], deposition of desert dust from Asia [Bishop *et al.*, 2002], and oceanic transport from the continental shelf [Lam *et al.*, 2006]. Typical mesoscale eddies in this region have 100-km radii [Crawford *et al.*, 2007], much smaller than the >1000-km wide August 2008 bloom. Also, eddy positions from satellite altimetry were unrelated to satellite chlorophyll in August 2008. Asian dust storms can reach North America in spring [Bishop *et al.*, 2002], but wind trajectories in late summer disfavor transport from Asia [Boyd *et al.*, 1998]. No dust storms were identified in late summer 2008, nor was dust from non-volcanic sources detected by the satellite ash analysis. Other eruptions, such as Okmok Volcano in July 2008 [Larsen *et al.*, 2009], showed weak ash signals confined near the volcano. Winter iron data and ocean transport modeling have demonstrated the potential for particulate iron transport from the continental shelf to the basin interior

at depth, where wintertime mixing can bring it to the surface [Lam *et al.*, 2006]. Dissolved iron measured at Station P in June 2008 had typically low summertime levels to 100 m (K. Johnson, unpublished data), demonstrating the absence of a subsurface iron reservoir in summer 2008. Seaglider temperature and salinity measurements show that the depth of the ocean mixed layer remained at 25–30 m throughout August 2008 at Station P, despite several storms. Even if a deep reservoir of iron had existed, it could not have reached the surface by storm-driven mixing.

[13] Early deep mixed layers may have delayed spring productivity, but not until August. Because of a colder winter, mixed layers were deeper in winter and early spring 2008 than typical [Freeland *et al.*, 1997]. However, temperature at the Station P mooring and profiling Argo floats in the subarctic NE Pacific showed that normal stratification was established by mid-May. Sunlight recorded by the Station P mooring and cloud fractions retrieved from the AIRS satellite show that summer 2008 had typical light intensities, so delay of early summer productivity by light restriction was not a factor in the bloom.

[14] High surface chlorophyll was also detected by satellite measurements in August 2008 in the subarctic NW Pacific centered along the shallow ridge to the west of the Aleutian Islands and near the Kamchatka Peninsula (Figures 1d and S1), but we suspect this high chlorophyll had a separate cause. The coastal areas in the East Kamchatka Current and along the Aleutian Islands ridge show pronounced spring blooms and are not iron-limited [Banse and English, 1999]. Late summer blooms in even the areas to the north and south of this ridge are not rare, with events in 1979, 1998, and 2004 [Banse and English, 1999; Sasaoka *et al.*, 2002; Yoo *et al.*, 2008]. No atmospheric iron sources (dust or ash) to the subarctic NW Pacific in August 2008 could be identified. Sasaoka *et al.* [2002] link the fall 1998 event in this region to high sea surface temperatures and enhanced stratification. August 2008 had very high surface temperatures in the subarctic NW Pacific (Figure S1), so enhanced stratification may have played a role in this western event, but without further observations we can only speculate.

#### 5. Implications

[15] The ~25  $\mu\text{atm}$  decrease in  $\text{pCO}_2$  at Station P implies a carbon drawdown of 0.3–0.7  $\text{mol-C m}^{-2}$  for this event, based on calculated dissolved inorganic carbon changes assuming a 30-m mixed layer and calcium carbonate formation of 0–0.5 times the organic carbon production (Emerson *et al.*, submitted manuscript, 2010). Because the surface was undersaturated with  $\text{CO}_2$ , gas exchange would have acted to raise the  $\text{pCO}_2$ , but this would affect our calculation by <10%. Extrapolating this Station P estimate to the  $1.5\text{--}2 \times 10^6 \text{ km}^2$  area of the bloom [Langmann *et al.*, 2010a] results in a potential 0.006–0.017 Pg-C drawdown.

[16] There is some evidence that much of the ~0.01-Pg C drawdown could have been exported from the surface ocean. Following the initial changes,  $\text{pCO}_2$  and pH remained stable, not beginning to return to pre-bloom values until mid-October when the mixed layer deepened. Surface NCP was higher than normal until at least 31 August, indicating net photosynthesis and export throughout the second half of August. Also, August and September 2008 mesozooplankton abundances, measured by Continuous Plankton Recorder

(CPR) surveys, were above the maximums measured in those months in 2000–2007 and 2009, and dominated by large copepods. Large copepods could not have responded to the bloom by reproducing, but the bloom may have caused them to feed closer to the surface where the CPR captured them. Large mesozooplankton would likely have enhanced export of organic matter from the bloom through repackaging in heavier fecal pellets. High diatom abundances would also have increased export by increasing the density of sinking particles.

[17] To our knowledge, the August 2008 subarctic NE Pacific bloom is the first directly observed, basin-scale, high-productivity event caused by iron fertilization from volcanic ash. This bloom was the largest event in the satellite chlorophyll time series for this region stretching back to 1997, mainly attributable to the large depositional area of the Kasatochi ash. However, carbon export by this bloom was relatively modest (~0.01 Pg C), just 0.5% of the roughly 2 Pg C of anthropogenic CO<sub>2</sub> taken up by the ocean each year [Manning and Keeling, 2006]. A synergistic combination of new observing technologies (in situ sensors, Seaglider, satellites) and time series cruises created an exceptional set of observations that elucidated the mechanism of this rare event. This natural iron fertilization complements purposeful iron enrichment experiments, providing observations of a fertilized area not subject to lateral dilution. The event will also serve as a comparison to other natural iron fertilizations (by dust for example) and as an analogue for the possible impact of large-scale purposeful iron fertilization.

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- S. D. Batten, Sir Alister Hardy Foundation for Ocean Science, 4737 Vista View Cr., Nanaimo, BC V9V 1N8, Canada.
- L. A. Coogan, K. E. Giesbrecht, D. S. Grundle, and R. C. Hamme, School of Earth and Ocean Sciences, University of Victoria, PO Box 3065 STN CSC, Victoria, BC V8W 3V6, Canada. (rhamme@uvic.ca)
- W. R. Crawford, J. F. R. Gower, M. A. Peña, and F. A. Whitney, Institute of Ocean Sciences, Fisheries and Oceans Canada, PO Box 6000, Sidney, BC V8L 4B2, Canada.
- M. D. DeGrandpre, Department of Chemistry and Biochemistry, University of Montana, 32 Campus Dr., Missoula, MT 59812, USA.
- S. R. Emerson, C. C. Eriksen, and D. Lockwood, School of Oceanography, University of Washington, Box 355351, Seattle, WA 98195, USA.
- M. T. Kavanaugh, College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, OR 97331, USA.
- C. L. Sabine, Pacific Marine Environmental Laboratory, NOAA, 7600 Sand Point Way NE, Seattle, WA 98115, USA.
- P. W. Webley, Geophysical Institute, Alaska Volcano Observatory, University of Alaska Fairbanks, 903 Koyukuk Dr., Fairbanks, AK 99775, USA.