Temporal variability of dissolved iron species in the mesopelagic zone at Ocean Station PAPA

Christina Schallenberg a,b,*, Andrew R.S. Ross c, Ashley B. Davidson a,d, Gillian M. Stewart e, Jay T. Cullen a

a School of Earth and Ocean Sciences, University of Victoria, PO Box 1700 Stn CSC, Victoria, BC V8W 2Y2, Canada
b Antarctic Climate & Ecosystems CRC, Private Bag 80, Hobart, TAS 7001, Australia
c Institute of Ocean Sciences, Fisheries & Oceans Canada, 9860 West Saanich Road, Sidney, BC V8L 4B2, Canada
d Department of Earth, Ocean and Atmospheric Sciences, University of British Columbia, 2207 Main Mall, Vancouver, BC V6T 1Z4, Canada
e Queens College and Graduate Center, City University of New York, Flushing, NY 11367, USA

ABSTRACT
Deposition of atmospheric aerosols to the surface ocean is considered an important mechanism for the supply of iron (Fe) to remote ocean regions, but direct observations of the oceanic response to aerosol deposition are sparse. In the high nutrient, low chlorophyll (HNLC) subarctic Pacific Ocean we observed a dissolved Fe and Fe(II) anomaly at depth that is best explained as the result of aerosol deposition from Siberian forest fires in May 2012. Interestingly, there was no evidence of enhanced dFe concentrations in surface waters, nor was there a detectable phytoplankton bloom in response to the suspected aerosol deposition. Dissolved Fe (dFe) and Fe(II) showed the strongest enhancement in the subsurface oxygen deficient zone (ODZ), where oxygen concentrations <50 μmol kg⁻¹ are prevalent. In the upper 200 m, dFe concentrations were at or below historic background levels, consistent with a short residence time of aerosol particles in surface waters and possible scavenging loss of dFe. Aerosol toxicity and/or dominance of particle scavenging over dissolution of Fe in the upper water column may have contributed to the lack of a strong phytoplankton response.

1. Introduction
Low availability of the micronutrient iron (Fe) limits primary production in about 40% of the surface ocean (Moore et al., 2002). High nutrient, low chlorophyll (HNLC) areas result where the low solubility of Fe in seawater and low rates of Fe supply conspire to limit the growth of marine phytoplankton (jickells et al., 2005; Liu and Millero, 2002; Martin et al., 1989), effectively causing what is commonly referred to as “iron limitation”. Iron limitation in HNLC regions reduces the efficiency of the biological carbon pump, thus diminishing the ocean’s ability to absorb carbon dioxide from the atmosphere (Martin, 1990; Sunda, 2010).

The surface waters of the remote HNLC northeast Pacific Ocean receive Fe from intermittent sources such as atmospheric deposition (Crusius et al., 2011; Duce and Tindale, 1991; Hamme et al., 2010) and the penetration of mesoscale eddies generated near shore (Brown et al., 2012; Johnson et al., 2005; Lippiatt et al., 2011; Xiu et al., 2011). Iron addition from these sporadic sources frequently enhances phytoplankton biomass and primary production in affected areas (Xiu et al., 2014; Hamme et al., 2010; Bishop et al., 2002).

Much of the research into the potential impact of aerosol deposition on oceanic biota has focused on the solubility of Fe in aerosols (e.g., Schroth et al., 2009; Buck et al., 2006; Sedwick et al., 2007; Sholkovitz et al., 2012). Combining this information with data on regional dust fluxes and assumed or measured Fe content of aerosols, it is possible to estimate the contribution of atmospheric deposition to dissolved Fe (dFe) concentrations in the global ocean (e.g., Duce and Tindale, 1991; Moore and Braucher, 2008; Tagliabue et al., 2009). Such estimates form the basis for models connecting dust deposition to ocean biogeochemistry and the Earth’s climate (e.g., Jickells et al., 2005; Watson et al., 2000), which frequently assume that aerosol deposition relieves Fe limitation and enhances phytoplankton growth. In the subarctic North Pacific Ocean, atmospheric Fe supply from dust deposition is estimated to contribute 0.01–0.03 mmol Fe m⁻² y⁻¹ (Moore and Braucher, 2008). This figure likely needs to be corrected upwards by a factor 2 or 3, as a recent analysis of core-top sediments has found that models significantly

* Corresponding author.
E-mail address: christina.schallenberg@utas.edu.au (C. Schallenberg).
underestimate dust deposition in the subarctic North Pacific (Serno et al., 2014).

The majority of dust reaching this oceanic region is thought to originate from Asia, particularly the arid regions of China (Uematsu et al., 1983; Mahowald et al., 2009; Tan et al., 2013), but aerosols from forest fires in Russia may also play an important role in contributing soluble Fe to the North Pacific Ocean (Ito, 2011). With plumes from Siberian forest fires observed as far east as the western United States and Canada (Bertschi et al., 2004; Cottle et al., 2014), it is likely that aerosols from such fires are sporadically deposited in all sectors of the North Pacific Ocean. However, little is known about the impact and fate of forest fire aerosols in oceanic waters.

In this paper, we present evidence of a dFe and Fe(II) anomaly in the oxygen deficient zone (ODZ) of the HNLC subarctic North Pacific Ocean at Ocean Station PAPA (OSP; 50°N and 145°W). Our analysis of possible external Fe sources suggests that the anomaly most likely resulted from the deposition of aerosols that stemmed from forest fires in Siberia.

2. Materials and methods

2.1. Dissolved Fe and Fe(II)

The methods for the measurement of dFe and Fe(II) in June 2012 and August 2013 are described in detail in Schallenberg et al. (2015). Briefly, dFe was measured on filtered (0.2 μm) and acidified (pH 1.8) samples using a modified flow injection analysis (FIA) method that relies on detection of Fe(III) with the chemiluminescent reagent luminol (de Jong et al., 1998; Obata et al., 1993). The historic dFe data from OSP were measured at sea by the Institute of Ocean Sciences in Sidney, Canada, on cruises in spring 2009, summer 2010 and spring 2011, on filtered samples (0.2 μm) that had been acidified to pH 1.8 for at least 12 h prior to measurement, following GEOTRACES protocols (Cutter et al., 2010). The analytical method was based on Obata et al. (1993). The VERTEX data were taken from Table A4 of the original publication and were measured using graphite furnace atomic absorption spectrophotometry on filtered (0.4 μm) samples that had been pre-concentrated using organic extraction (Martin et al., 1989).

Iron(II) was determined within minutes of sample collection from GO-FLO bottles using the luminol method and a custom-made FIA system without an injection valve or pre-concentration, following the approach of Hansard and Landing (2009) but without acidification of the sample.

2.2. Dissolved oxygen and Fe(II) half-life

Dissolved oxygen concentrations were measured with a Sea-Bird Electronics dissolved oxygen sensor (SBE 43) on the CTD package of the CCGS John P. Tully in June 2012. The oxygen sensor was calibrated with discrete dissolved oxygen data following Institute of Ocean Sciences protocols. The calculation of Fe(II) half-life is described in detail in Schallenberg et al. (2015).

2.3. Sea surface height anomaly

The sea surface height anomaly (SSHA) image for June 3 was downloaded from the Colorado Center for Astrodynamics Research (CCAR) Global Historical Gridded SSHA Data Viewer website. The SSHA product merges data from multiple altimetry satellites.

2.4. Profiling float

Quality-controlled data for profiling float 7601StnP were downloaded from http://www.mbari.org/chemsensor/FloatViz.htm. The float was equipped with a WETLabs fluorometer/backscatter sensor (ECO FLbb-AP2) and an in situ ultraviolet spectrophotometer (ISUS) for nitrate measurements (Johnson and Coletti, 2002). Floats are programmed to profile the upper 1000 m of the water column every 5–6 days.

Chlorophyll a concentrations were estimated from fluorescence measurements using the scale factor supplied by the manufacturer as follows: Chlorophyll a [μg L⁻¹] = (sensor output – dark counts) [counts] * scale factor [μg chl a L⁻¹ count⁻¹]. No attempt was made to correct for daytime fluorescence quenching.

2.5. UV Aerosol Index

UV Aerosol Index data were downloaded from the Giovanni OMI/Aura Online Visualization and Analysis website. The UV Aerosol Index is calculated based on the difference between observations and model calculations of spectral radiance ratios in the UV (see http://disc.sci.gsfc.nasa.gov/data-holdings/PIP/aerosol_index.shtml). This index indicates the presence of aerosols such as dust and soot that absorb in the UV.

2.6. Silicic acid and chlorophyll a

Silicic acid (Si(OH)₄) concentrations were measured on fresh samples at sea using a Technicon AutoAnalyzer (Strickland and Parsons, 1972; Barwell-Clarke and Whitney, 1996). Samples for discrete chlorophyll a analysis were filtered onto Whatman GF/F filters and extracted with 90% acetone prior to fluorometric analysis (Strickland and Parsons, 1972).

Additional methods are outlined in the supporting information.

3. Deep anomaly in dFe and Fe(II) concentrations

The dFe data for Ocean Station PAPA (OSP) from June 3, 2012, show an anomaly at depth relative to historic data (Fig. 1A and B and Tables 1 and 2 in the SI). The anomaly is most pronounced in the depth range 400–1000 m, with the highest dFe and Fe(II) concentrations in the ODZ. Below 100 m depth, Fe(II) concentrations follow the same trend as dFe, exhibiting an increase with depth that is well above Fe(II) concentrations measured at other offshore stations in the HNLC subarctic Pacific on the same cruise (Fig. 1B; station locations are indicated in Fig. 2). The observed Fe(II) concentrations below 100 m are also significantly higher than the median values reported by Hansard et al. (2009) for two transects in the eastern North Pacific (their Fig. 5B and C). While Hansard et al. (2009) found that Fe(II) concentrations in the 150–600 m depth range were typically below 12 pM, Fe(II) at OSP in June 2012 increased from 10 pM at 150 m to 50 pM at 500 m, with the maximum Fe(II) concentration (72 pM) observed at 800 m. The increase in Fe(II) with depth corresponds to decreasing dissolved oxygen concentrations and longer Fe(II) half-lives (Fig. 1C), suggesting that a near-constant Fe(II) supply with depth, e.g. from a particulate Fe source, could lead to the observed distribution. The relatively high Fe(II) concentrations at depths shallower than 100 m are likely the result of photochemical production in the sunlit surface layer (Rijkenberg et al., 2005; Barbeau et al., 2001) and were not considered further in this investigation.

4. Possible causes for deep dFe and Fe(II) enhancement

The principal external sources of dFe and particulate Fe to the NE subarctic Pacific Ocean include the passage of mesoscale eddies generated near shore (Brown et al., 2012; Johnson et al., 2005; Lippiatt et al., 2011), isopycnal transport from the continental margins (Lam and Bishop, 2008; Lam et al., 2006), and atmospheric deposition of aerosols (Bishop et al., 2002; Crusius et al., 2011; Hamme et al., 2010).
4.1. Passage of a mesoscale eddy

Eddies frequently penetrate deep into the NE subarctic Pacific Ocean (Xiu et al., 2011), transporting particulate and dissolved Fe well above background concentrations for the surrounding open-ocean waters (Johnson et al., 2005). This Fe signature can be observed up to 20 months into an eddy’s lifetime (Johnson et al., 2005) and is at least partly responsible for the elevated chlorophyll a (chl a) concentrations that are frequently associated with eddies in the NE subarctic Pacific (Crawford et al., 2007; Xiu et al., 2014). However, there is no evidence that an eddy was present at OSP in June 2012. The shipboard CTD data show no indication of depressed or elevated isopycnals, and satellite images of sea surface height anomaly (SSHA) do not suggest that an eddy was present at or near OSP in June 2012 (Fig. 2). Furthermore, Argo data for floats in the vicinity of OSP between April 1 and July 1, 2012, do not show any trajectories that would be consistent with an eddy, and the same is true for an APEX float that was released at OSP in early 2012 (see inset in Fig. 3). The float stayed in the vicinity of OSP from early 2012 well into 2013, allowing for year-to-year comparison of the recorded nitrate and chlorophyll fluorescence data. There is only minimal nitrate drawdown in May 2012 compared to considerable drawdown in May 2013, and chl a fluorescence is also low in May 2012 compared to 2013 (Fig. 3). This is consistent with very limited phytoplankton growth at OSP in May 2012, contrary to expectations for an eddy.

Likewise, the surface macronutrient data measured on discrete samples in June 2012 (nitrate, phosphate and silicic acid) do not show any sign of a deficit relative to the historic average (silicic acid shown in Fig. 1 in SI). Discrete chl a concentrations measured at OSP in June 2012 were also unremarkable (0.4–0.6 mg L⁻¹) and below the historical average (Fig. 1 in SI), and Mackinson et al. (2015) report net primary production rates of <50 mmol m⁻² d⁻¹ at OSP in June 2012, compared to 79–105 mmol m⁻² d⁻¹ in June 2011. The weight of the evidence thus suggests that an eddy is an unlikely candidate for the cause of the deep dFe and Fe(II) anomaly observed in June 2012.

4.2. Subsurface advection from the continental shelf

It is also highly unlikely that the Fe enhancement observed to a depth of 1000 m stems directly from the continental margins. Particulate Fe hot spots presumably sourced from the Aleutian arc have previously been observed at OSP, but their maximum concentration was found around 200 m (Lam et al., 2006). The depth distribution was similar in both February and May, and a modelling exercise indicated that this Fe supply is carried by the general circulation in the Gulf of Alaska and does not extend below ~200 m (Lam et al., 2006). It is thus unlikely that this Fe source is directly responsible for the deep dFe and Fe(II) anomaly observed at OSP in June 2012. However, it is possible that increased aggregation following an aerosol deposition event to the surface ocean could have entrained particulate Fe from this continental source and led to increased export to depth (see Section 4.3).

The continental margin in the western subarctic Pacific has also been identified as an Fe source to the HNLC North Pacific Ocean (Lam and Bishop, 2008). However, its influence is not likely to reach as far as OSP, as transport times along isopycnals are estimated at
6–14 years (Ueno and Yasuda, 2003). Even though the eastern continental slope is closer to OSP in distance, sedimentary Fe input from this source is not detectable beyond a few hundred kilometres from shore (Schallenberg et al., 2015) and is therefore also an unlikely source for the observed Fe anomaly at OSP.

4.3. Aerosol deposition

The averaged daily UV aerosol index from the satellite-mounted Ozone Monitoring Instrument (OMI) for a 4×10° area centred at OSP shows a local maximum in early May 2012 (Fig. 4) that is well above the seasonal average, indicating the presence of UV-absorbing aerosols such as dust and soot. Decline of the UV aerosol index for areal bins along a southwest-to-northeast trajectory (i.e., the most likely direction of transport for this aerosol cloud based on back- and forward-trajectories, see Fig. 2 in SI) indicates that aerosol deposition to the ocean is a possibility (cf. Bishop et al., 2002). An investigation into the origin and movement of the aerosol cloud suggests that the material likely stemmed from forest fires in Siberia (Fig. 5). Aerosols from Siberian forest fires are frequently transported across the Pacific Ocean between April and August (e.g., Bertschi et al., 2004; Cottle et al., 2014; Tomshin and Solovyev, 2014), and deposition of aerosols from biomass burning to the ocean has been proposed to constitute an important localized source of soluble Fe (Guieu et al., 2005; Ito, 2011; Luo et al., 2008). Wet deposition co-occurring with precipitation is a common mode of aerosol delivery to the ocean (Raiswell and Canfield, 2012; Schlosser et al., 2014). The NOAA-PMEL mooring at OSP [http://www.pmel.noaa.gov/ocs/data/disdel_v2/disdel_v2.html] detected precipitation as well as a decrease in sea surface salinity on May 10–11, 2012, coincident with the passage of the aerosol cloud (Fig. 3 in SI).

Another piece of evidence consistent with an aerosol deposition event at OSP in spring 2012 comes from 234Th measurements reported by Mackinson et al. (2015), suggesting high particle export in June 2012. Mackinson and colleagues deployed sediment traps at OSP for ~3 days in June 2012 and found 234Th fluxes close to 4000 dpm m−2 d−1 at 200 m. This flux is almost twice as high as the 234Th flux measured at the same location, with the same traps, in June 2011 (Mackinson et al., 2015), and is more than twice as high as the 234Th flux measured in sediment traps at station K2 in the northwest Pacific Ocean in July 2005 (Buesseler et al., 2009). The ratio of particulate organic carbon (POC) to 234Th of the particles intercepted at 200 m was only 1.3 in June 2012, compared to 3.7 in June 2011, indicating that the sinking material in June 2012 contained a higher fraction of inorganic matter relative to the biogenic flux, which was similar in magnitude to June 2011 (Mackinson et al., 2015). The combination of increased flux with higher inorganic particle content is consistent with the surface deposition and subsequent sinking of lithogenic material.

5. From aerosol deposition to dFe at depth

Several studies investigating the effect of aerosol deposition (e.g., dust or volcanic ash) in the HNLC subarctic Pacific Ocean have focussed on surface effects, such as enhanced phytoplankton biomass (e.g., Hamme et al., 2010; Bishop et al., 2002; Tan et al., 2013). Much less is known about the fate of aerosols, and aggregates of aerosols, as they sink through the water column. However, there is evidence from the ODZ in the tropical North Atlantic Ocean that mineral dust input from the Sahara leads to elevated dFe concentrations in the depth range 200–800 m, i.e. at the heart of the ODZ (Fitzsimmons et al., 2013; Measures et al., 2008). The authors attribute this enhancement to the remineralization of particulate material with high Fe:C ratios. Although this material is presumed to be of biological origin, and thus an indirect consequence of relieved Fe limitation in surface waters due to aerosol deposition from the Saharan dust plume, it is not possible with the available data to distinguish between organic and inorganic particles as a source for the dFe enhancement.
As discussed above, there was no evidence of enhanced chl a concentrations at OSP in May and June 2012 (i.e., compared to the seasonal average) based on analysis of shipboard samples and float data. Likewise, MODIS satellite imagery for May 2012, covering a much larger area of the NE subarctic Pacific, shows no sign of elevated chl a (Fig. 4 in SI). It thus appears that the presumed aerosol deposition event in May 2012 did not elicit a strong phytoplankton response. We discuss possible reasons for this observation below. The implication in the context of the deep dFe enhancement observed at OSP in June 2012 is that if the excess dFe resulted from an aerosol deposition event, then it was likely a direct consequence of the dissolution of deposited material, rather than stemming from the remineralization of a sinking phytoplankton bloom. This interpretation is consistent with a high proportion of inorganic material found in sediment traps at OSP in June 2012 (Mackinson et al., 2015).

Little is known about the composition of aerosols from forest fires with respect to Fe concentrations and solubility. A modelling study by Ito (2011) indicates that emissions from Siberian forest fires could supply soluble Fe to the ocean. The most likely source of Fe would be dust particles entrained in the forest fire plume, which are then subjected to acidic processing (Hsu et al., 2010a; Ito, 2011; Ito and Shi, 2016). Indeed, field evidence from biomass burning in the African Savanna has shown that pyro-convection in large fires frequently causes the entrainment of dust and soil particles into the aerosol cloud (Gaudichet et al., 1995), and that Fe solubility of internally mixed dust is increased in aerosols that are impacted by biomass burning (Hsu et al., 2010b; Ito and Shi, 2016; Paris et al., 2010). Observations from forest fire emissions in the Mediterranean suggest that the aerosols have a 2% fractional Fe solubility (Guieu et al., 2005), while Australian aerosols influenced by bush fires show fractional Fe solubilities ~3% (Winton et al., 2016). It is thus likely that the material deposited at OSP contained both crustal particles and aerosols directly originating from biomass burning, with fractional Fe solubility at least equal to, and possibly higher than that of lithogenic particles not impacted by biomass burning.

So how realistic is it that the deep Fe enhancement measured on June 3, 2012, stemmed from settling particles that were delivered to the surface ocean around May 12? Following dust deposition in the oligotrophic North Atlantic, particle-settling velocities in the range 32–44 m d$^{-1}$ have been observed (e.g., Brust et al., 2011; Neuer et al., 2004), while estimates from artificial dust seeding experiments span from ~24 to 86 m d$^{-1}$ (Bressac et al., 2012). For the dFe maximum measured at 800 m on June 3 to result from dissolution of particles that were deposited on May 12, a particle settling velocity of ~36 m d$^{-1}$ is required, consistent with the data from the literature. The deep dFe enhancement evident in the presented data could therefore result from the dissolution of sinking Fe-containing particles.

Investigating the cycling of lithogenic marine particles in the North Atlantic, Ohnemus and Lam (2015) observed fast removal of particles from the mixed layer and a relatively constant distribution of small particles below 300 m. Based on estimated aerosol dust
Aerosol samples from the North Pacific have been found to contain a significant fraction of Fe(II) (Buck et al., 2013). Dissolution of such Fe(II)-containing particles and/or a reductive dissolution mechanism of the particles, possibly enhanced by the low oxygen concentrations in the ODZ, could produce the observed Fe(II) profile at OSP in June 2012. The decreasing oxygen concentrations with depth would stabilize Fe(II) against oxidative loss, leading to increased Fe(II) concentrations with depth (Fig. 1). However, oxygen concentrations at OSP are not low enough to support the long-term presence of Fe(II); they are merely low enough to slow oxidation (Fig. 1C). Iron(II) derived from sinking particles is therefore expected to ultimately feed into either the dFe or particulate Fe pool, depending on the availability of stabilizing Fe ligands (Johnson et al., 1997). It is thus not surprising that the shape of the dFe profile at OSP in June 2012 mirrors the shape of the Fe(II) profile (Fig. 1). However, we cannot distinguish with the present data whether the observed Fe speciation reflects the speciation present in the parent aerosol, or whether it is the result of reductive processes associated with the particles. Such processes could be directly related to the low oxygen concentrations in the ODZ, and/or they may be mediated by microbes associated with the sinking particles.

6. Lack of a strong biological response to aerosol deposition

As outlined above, there is no evidence that the suspected aerosol deposition event triggered a phytoplankton bloom. There are several possible explanations for this observation, including deep mixing or subduction of the water mass that received the aerosol deposition. For example, Fe limitation might have been temporarily relieved as a result of the deposition event but primary productivity would likely still have been hampered by insufficient light due to a relatively deep mixed layer on May 12 (~60 m, Fig. 3 in SI), resulting in low chl a standing stock and nitrate drawdown. After May 12, warming of the sea surface led to increased stratification and shallower mixed layers (Fig. 3 in SI), but nitrate drawdown remained low until later in the season (Fig. 3). There were no strong wind events recorded in May 2012 at OSP, and no mesoscale eddies were present within a radius of several hundred kilometres (Fig. 2 and Fig. 3 in SI). Subduction is therefore an unlikely explanation for the absence of a strong biological response, but deep mixing could have limited primary productivity during and shortly after the deposition event.

It is possible that the resident phytoplankton, even without an observable increase in chl a standing stocks, rapidly took up any dFe that might have been added to the surface ocean as a result of aerosol deposition. Iron-starved phytoplankton significantly increase their Fe-uptake rates, allowing them to take maximum advantage of sporadic Fe pulses (Harrison and Morel, 1986). Rapid Fe-uptake would have reduced dFe in surface waters, but it does not explain the observed low dFe concentrations to a depth of ~200 m in June 2012 (Fig. 1).

6.1. Particle scavenging in surface waters

Studies focussing on the biological effects of aerosol deposition have implied that deposition events resulted in Fe addition to surface waters (e.g., Hamme et al., 2010; Bishop et al., 2002; DiTullio and Laws, 1991; Young et al., 1991), but direct measurements to that effect are rare and their results are inconclusive. There is evidence that the scavenging effect of aerosols deposited to the surface ocean may dominate over Fe dissolution in certain situations (e.g., Rogan et al., 2016; Crook et al., 2004). For example, Rogan et al. (2016) found
that after the eruption of the Eyjafjallajökull volcano in Iceland in 2010, Fe scavenging by the high particle load mitigated the Fe fertilizing effect of the ash deposition. Likewise, Croot et al. (2004) report very short residence times for dissolved and particulate Fe in surface waters of the equatorial North Atlantic after dust deposition from the Sahara, suggesting that added Fe is rapidly removed by scavenging, aggregation and sinking. In the same region but in a different year, Rijkenberg et al. (2008) observed only a slight dFe enhancement following a Saharan dust event, with concentrations increasing from 0.20 (initial) to 0.25 nM.

Mesocosm studies have found that seeding with atmospheric dust may decrease the dFe inventory in surface waters (Wagener et al., 2010; Wuttig et al., 2013), presumably due to scavenging onto sinking particles (Ye et al., 2011). These mesocosm studies were carried out in Fe-replete waters, so their results may not be directly applicable to the HNLC subarctic ocean, where dFe concentrations are generally low. However, dominance of particle scavenging over dissolution in the upper water column, where particle aggregation and subsequent export are most pronounced (Ohnemus and Lam, 2015), could explain the low dFe concentrations (<0.2 nM) to a depth of 200 m at OSP in June 2012 (Fig. 1A), and it could also explain the absence of a strong biological response to the proposed aerosol deposition event.

6.2. Aerosol toxicity

Another possibility is that the aerosols had an adverse effect on the biota, as was observed in several studies with African aerosols (Hill et al., 2010; Paytan et al., 2009). Hill et al. (2010) report metabolic impairment of Prochlorococcus in response to dust addition during incubation experiments in the tropical northeast Atlantic Ocean. In a similar experiment conducted in the northern Red Sea, Paytan et al. (2009) observed toxic as well as fertilizing effects from African aerosols, with differential responses in different phytoplankton taxa. Given the limited information available regarding the elemental composition of forest fire aerosols, we refrain from speculating about the toxic elements that might be responsible for an adverse effect on phytoplankton. Suffice it to say that it is possible that aerosol toxicity could have prevented a phytoplankton bloom, but other factors, such as particle scavenging discussed above, are at least equally likely.

7. Conclusions

The depth distributions of dFe and Fe(II) at OSP observed in June 2012 are consistent with recent external input of Fe. Even though the dFe and Fe(II) maxima are found at 800 m, the available evidence suggests that an aerosol deposition event, probably stemming from forest fires in Siberia, is the most likely source of the Fe. Contrary to expectations, it does not appear that the Fe input was the result of remineralization, as there was no indication of a phytoplankton bloom in response to the aerosol deposition. Rather, the data suggest that the elevated dFe and Fe(II) concentrations in the ODZ resulted directly from the slow dissolution of aerosol particles and/or dissolution of lithogenic particles scavenged by aerosols, with a possible role for reductive processes enhancing dissolution at lower oxygen concentrations. This interpretation is consistent with the observations by Measures et al. (2008) and Fitzsimmons et al. (2013) for the ODZ in the tropical North Atlantic Ocean underlying the Saharan dust plume, where elevated dFe concentrations coincide with low oxygen concentrations in the water column.

Explanations for the absence of a phytoplankton bloom in response to the suspected aerosol deposition include light limitation, lack of Fe fertilization in surface waters and toxic effects of the aerosol on the phytoplankton community. With the present data it is impossible to pinpoint the exact cause, in part because little is known about the composition of aerosols from forest fires, especially with respect to trace metal concentrations. However, the observed depth distribution of dFe suggests that the aerosols deposited in the NE subarctic Pacific in May 2012 likely had a short residence time in the surface ocean, evident in the lack of elevated dFe concentrations in the upper 200 m of the water column.

Our observations illustrate that the impact of aerosol deposition events on surface ocean biology depends strongly on aerosol composition and fate. A similar point has been made by Boyd et al. (2010), who estimated that the expected dFe addition from dust deposition events was often insufficient to cause a phytoplankton bloom, and that observed biological signatures were falsely attributed to dust deposition. Clearly, the links between aerosol deposition, alleviation of Fe limitation, and phytoplankton responses deserve further investigation. In particular, research is needed on how factors such as scavenging, aerosol source and atmospheric processing control the impact of aerosol deposition on ocean biogeochemistry.
Appendix A. Supplementary data

Barwell-Clarke, J., Whitney, F., 1996. Institute of Ocean Sciences Nutrient Methods and may be requested from Andrew Ross (Andrew.Ross@dfo-mpo.gc.ca); OSP were generated by W. Keith Johnson and Nes Sutherland and the national programs that contribute to it. Historic dFe data from were made freely available by the International Argo Program and Johnson, K.S., Gordon, R.M., Coale, K.H., 1997. What controls dissolved iron concentrations in the world ocean? Mar. Chem. 57, 137–161.http://dx.doi.org/10.1016/S0304-4401(97)00026-9.

References


