

Geochemical evidence of oceanic iron fertilization by the Kasatochi volcanic eruption in 2008 and the potential impacts on Pacific sockeye salmon

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ABSTRACT: The Kasatochi volcanic eruption that occurred in the central Aleutian Islands in Alaska, USA, in August 2008 is thought to have induced a massive diatom bloom in the iron-limited waters of the Gulf of Alaska, which potentially affected the oceanic food web by increasing the abundance of zooplankton and sockeye salmon *Oncorhynchus nerka* in the northeast Pacific Ocean. We report the first seawater experiments involving volcanic ash ejected from the Kasatochi eruption, showing that the ash released 61 to 83 nmol Fe, 374 to 410 nmol NO₃⁻, 5 to 6 nmol PO₄³⁻ and 170 to 585 nmol SiO₂ when it contacted seawater. Our study suggests that the amount of iron released from Kasatochi ash (an increase of 2.0 to 2.8 nM Fe) was indeed sufficient to cause the observed phytoplankton bloom in the northeastern Pacific Gyre, while the impact of macronutrient release was minimal. We further evaluated the multiple, interdependent processes in the oceanic food web related to the diatom bloom, involving the ocean survival of juvenile salmon that entered the northeast Pacific Ocean in the summer of 2008.

KEY WORDS: Kasatochi eruption · Volcanic ash · Fe limitation · Diatom bloom · Gulf of Alaska · Sockeye salmon

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INTRODUCTION

Volcanic ash ejected during explosive volcanic eruptions can be transported several hundreds of kilometers in the atmosphere and deposited in the remote ocean, where nutrient levels in the surface ocean limit marine primary productivity. Upon interaction with seawater, volcanic ash releases several biologically relevant elements into the seawater (Frogner et al. 2001, Duggen et al. 2007, Jones & Gislason 2008, Olgun et al. 2011, 2013) which may affect

phytoplankton growth (Censi et al. 2010, Hamme et al. 2010, Langmann et al. 2010b, Lin et al. 2011, Hoffmann et al. 2012). Some eruptions can negatively affect the marine environment by releasing acidic aerosols and thus reducing the pH of the seawater (Wall-Palmer et al. 2011), or releasing toxic metals (e.g. Cu) in high concentrations (Frogner Kockum et al. 2006, Hoffmann et al. 2012).

The northeast Pacific Ocean is a high-nutrient, low-chlorophyll (HNLC) ocean region where phytoplankton growth is known to be limited by Fe (Martin

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& Fitzwater 1988, Boyd & Harrison 1999), and sporadically by Si (Wong & Matear 1999, Whitney et al. 2005). It is one of the most volcanically active regions on Earth, containing more than 150 subaerial volcanoes in the Kurile-Kamchatka and Aleutian volcanic arcs, which produce about 10 volcanic eruptions each year (Siebert & Simkin 2002). Due to the high flux of volcanic ash in the North Pacific Ocean, atmospheric deposition of volcanic ash has been considered to be an important external Fe source in the region (Olgun et al. 2011). The fertilizing potential of volcanic eruptions has been previously observed in the North Pacific Ocean region after the eruptions of Miyake-Jima in 2000 and Anatahano in 2003 (Uematsu et al. 2004, Lin et al. 2011), and also in the neighboring rivers and lakes during the Mount St. Helens eruption in 1980 (Smith & White 1985).

During July–August 2008, 3 explosive volcanic eruptions occurred in the remote Aleutian Islands of Alaska: at Okmok on 12 July, Cleveland on 21 July, and Kasatochi on 7 to 8 August (Waythomas et al. 2008, Larsen et al. 2009, Langmann et al. 2010b). The Kasatochi volcanic eruption was the largest of the 3 eruptions, producing several ash plumes that reached as high as 18 km above the sea level (Langmann et al. 2010a, Waythomas et al. 2010). An un-

usual and extensive phytoplankton bloom (covering an area of ca. 1.5×10^6 km²) started in the Gulf of Alaska a few days after the Kasatochi eruption (Fig. 1), and this bloom has been related to Fe-fertilization by Kasatochi ash fallout (Hamme et al. 2010, Langmann et al. 2010b). The mean chlorophyll *a* (chl *a*) values in August 2008 were 2 to 3 times higher than the usual values for this time of year (Hamme et al. 2010).

The phytoplankton bloom that started a few days after the eruption was detectable by satellite images for over 2 mo, until the end of September 2008 (Hamme et al. 2010, Langmann et al. 2010b). Two years after the Kasatochi eruption, a record number (35 million) of sockeye salmon *Oncorhynchus nerka* returned to the Fraser River in Canada (Larkin 2010), causing scientists to speculate about possible reasons behind this dramatic number—including the effects of the volcanic eruption (Parsons & Whitney 2012).

Other potential nutrient sources in the region, such as wind-blown dust from Asian deserts or mesoscale eddies (which can provide nutrients from deep water), were lacking during the time of the diatom bloom; supporting the speculation of a link between the Kasatochi ash fallout and the subsequent phytoplankton bloom in the eastern North Pacific (Hamme

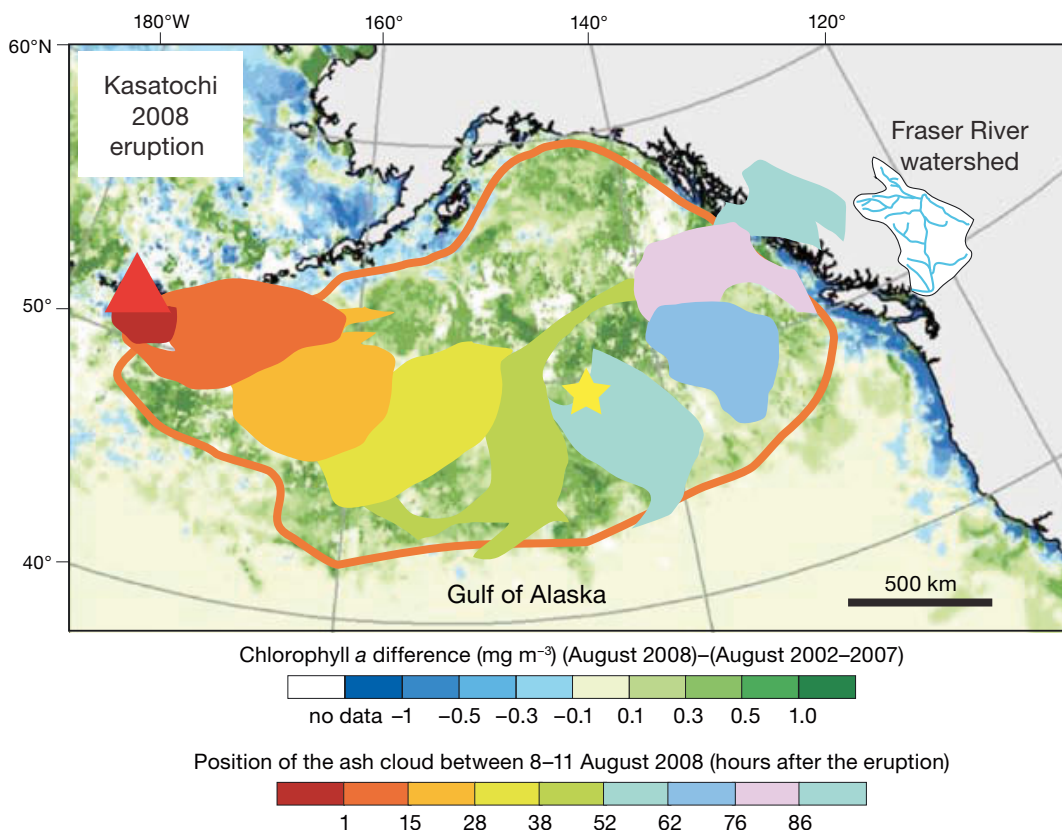


Fig. 1. MODIS-Aqua map based on Langmann et al. (2010b) showing relative increase in chlorophyll *a* concentrations in August 2008, most likely related to the Kasatochi (red triangle) volcanic eruption on 7 and 8 August 2008. The position of the ash cloud is shown in the colored areas. The bloom area is indicated by a red line. Chlorophyll *a* concentrations are the monthly mean August 2008 minus the background monthly mean in the last 6 yr (from August 2002 to August 2007). Also shown are the location of Ocean Station Papa (yellow star at 50°N, 145°W) and the Fraser River watershed area on the Pacific coast of Canada

et al. 2010, Langmann et al. 2010b). However, this possible link remained speculative as it was unknown if the Kasatochi eruption released sufficient amounts of Fe into the seawater. We present data from Fe- and macronutrient-dissolution experiments conducted using volcanic ash from the Kasatochi 2008 eruption. We further discuss the potential oceanic food-web dynamics affected by the Kasatochi eruption that might have influenced the salmon population in 2010 in the northeastern Pacific Ocean and also the neighboring rivers in the USA and Canada.

MATERIALS AND METHODS

Most of the volcanic ash ejected during the Kasatochi eruption was deposited in the ocean (Waythomas et al. 2010). Deposits on the Kasatochi and neighboring islands, which were readily available, had been exposed to rain and were wet when sampled (Waythomas et al. 2010). A fishing boat transiting the area during the eruption on 7 August, about 13 km southwest of the Kasatochi Island, received heavy ash fall. Crew members on the boat collected dry samples and provided them to the Alaska Volcano Observatory. The sample analyzed in the present study came from this fishing boat (Waythomas et al. 2010). The grain size of the sample was relatively coarse, and composed of particles greater than ash size (ash size is <2 mm). We wished to analyze the fine fraction of the tephra deposit, and separated the coarser fraction using 2 mm metal-free plastic sieves.

The release of Fe from Kasatochi ash was measured by means of cathodic stripping voltammetry (CSV) following the same method previously used by Duggen et al. (2007) and Olgun et al. (2011). Seawater samples used in the Fe-release experiments were from the eastern equatorial Atlantic Ocean, collected during Meteor cruise M68-3. The pH of the seawater was buffered at pH 8.0 by using 200 μl 4-(2-hydroxyethyl)-1-piperazinepropanesulfonic acid (EPPS) pH buffer at the clean laboratory. An artificial Fe-binding organic ligand (20 μl of TAC) was added to the seawater before the measurements (Croot & Johansson 2000). An ash sample (50 mg) was added into 200 μl seawater (mixing ratio of 2.5 g l^{-1}) and the measurements were done *in situ* in seawater using CSV. The measurements were done for 3 sub-samples (Fig. 2). The net release of Fe was converted to release in nanomoles g^{-1} of Kasatochi ash (Fig. 2).

The release of NO_3^- , NH_4^+ , NO_2^- , PO_4^{3-} and SiO_2 was performed by leaching experiments: 1 g of ash was added to 50 ml of Atlantic seawater in 60 ml

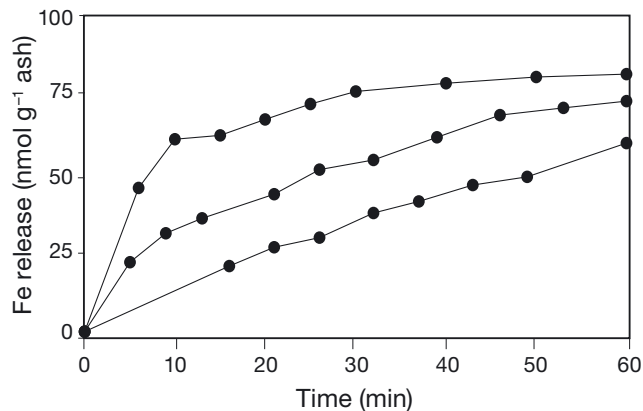


Fig. 2. Release of Fe from volcanic ash from the Kasatochi 2008 eruption in natural seawater over time. The 3 lines represent measurements of 3 sub-samples from the same volcanic ash sample. Measurements were done using cathodic stripping voltammetry

Nalgene Polypropylene plastic bottles (mixing ratio of 20 g l^{-1}) and shaken gently for about 20 min and then agitated for 1 h or 20 h in seawater. The solutions were later filtered rapidly through a 5 μm mesh plastic filter (PTFE Sartorius). Macronutrient concentrations in seawater were measured by standard routine photometry. The measured concentrations were converted to the release of nutrient in nanomoles g^{-1} of Kasatochi ash (Table 1). Total fixed nitrogen was expressed as NO_3^- . The release of NH_4^+ and NO_2^- was converted to NO_3^- by using molecular weights ($\text{NH}_4^+ = 32.01 \text{ g mol}^{-1}$, $\text{NO}_2^- = 60.01 \text{ g mol}^{-1}$, $\text{NO}_3^- = 76.01 \text{ g mol}^{-1}$). The measured concentrations of macronutrients were converted to the release of nutrient in nanomoles g^{-1} of Kasatochi ash (Table 1).

RESULTS

Fe-release measurements showed that Kasatochi ash mobilized ~61 to 83 nmol Fe g^{-1} ash within 1 h of contact with seawater (Fig. 2). This Fe-release range from Kasatochi ash is in the lower third of the range (35 to 340 nmol g^{-1} ash) for ash from subduction zone volcanoes like Kasatochi (Duggen et al. 2007, Olgun et al. 2011). The results of the macronutrient experiments showed that within the first hour of contact with seawater, Kasatochi ash released 374 nmol NO_3^- (as total fixed-N), 5 nmol PO_4^{3-} and 170 $\text{nmol of SiO}_2 \text{ g}^{-1}$ ash (Table 1). After 20 h, 410 nmol NO_3^- , 6 nmol PO_4^{3-} and 585 nmol of SiO_2 were released per gram of ash (Table 1). The highest leaching rates were seen for NO_3^- and SiO_2 , while the concentration of PO_4^{3-} stayed constant during the 20 h experiment. The data

Table 1. Estimated new supply of nutrients in the northeast Pacific Ocean related to the Kasatochi volcanic ash fallout in August 2008, based on the nutrient release from Kasatochi ash into seawater

	Release of nutrients from Kasatochi ash (nmol g ⁻¹ ash)	Initial seawater concentrations in the northeast Pacific Ocean (nM)	New supply of nutrients by the Kasatochi ash fallout (nM) ^c
Fe	61–83	<0.05 ^a	2.0–2.8 ^d
NO ₃ ⁻	374–410	5000–10 000 ^b	13–14
PO ₄ ³⁻	5–6	100–1000 ^b	<0.2
SiO ₂	170–585	5000–15 000 ^b	6–20

^aSource: Nishioka et al. (2001)
^bSource: Levitus et al. (1994), De Baar & De Jong (2001), Tsuda et al. (2003), Boyd et al. (2007)
^cBased on the nutrient release from Kasatochi ash calculated over the fertilized area of 1.5×10^6 km² in the Gulf of Alaska (Fig. 1) and a mixed layer of 20 m (www.pac.dfo-mpo.gc.ca/science/oceans/data/projects/argo/MLD/Mld2784.gif)
^dAbove the threshold (of 2 nM Fe) for stimulating diatom bloom in the Fe-limited regions (Wells 2003)

likely reflect a minimum, since the ash sample was coarse and collected near the Kasatochi volcano (i.e. within 13 km). Small particle size and interaction with cloud water during atmospheric transportation could enhance the solubility of surface compounds, and enhance the nutrient release of volcanic ash particles in the seawater (Duggen et al. 2010).

DISCUSSION

Potential nutrient supply by Kasatochi volcanic ash fallout

The background macronutrient concentrations in the eastern North Pacific range between 5–10 μ M NO₃⁻, 0.1–1 μ M PO₄³⁻ and 5–15 μ M SiO₂ (Levitus et al. 1994, De Baar & De Jong 2001, Tsuda et al. 2003, Boyd et al. 2007), whereas dissolved Fe concentrations are very low (<0.05 nM) (Levitus et al. 1994, Nishioka et al. 2001). External input of even nanomolar amounts of Fe can therefore have large impacts on marine primary production in the Fe-depleted waters of the northeast Pacific Ocean. The large increase in the phytoplankton stock would be accompanied by strong utilization of macronutrients, to a greater extent in the North Pacific than in other HNLC regions (Tsuda et al. 2003). A high demand for silica in the fertilized region of the eastern North Pacific was evidenced by reduced silicic acid concentrations during August 2008 (Hamme et al. 2010).

The increase of nutrient levels in the ash-fertilized region can be inferred from combining these new data (Table 1) with constraints for the erupted mass of $\sim 10^{15}$ g ash based on a 1-dimensional volcanic mo-

del (Langmann et al. 2010b), the area of the ash fall region of 1.5×10^6 km² (Fig. 1), and the ocean mixed layer depth of 20 m (www.pac.dfo-mpo.gc.ca/science/oceans/data/projects/argo/MLD/Mld2784.gif). The major error in the nutrient supply estimates comes from the actual volume of the ash deposit, which is unknown since most of the ash was deposited in the ocean. Satellite data indicate ash aloft over a broad area (Hamme et al. 2010, Langmann et al. 2010a,b), but this does not mean that the ash fallout occurred in the same area, and the ash fallout would have been non-uniform over the fertilized area. Also, the maximum increase in the Fe concentrations that could be reached in the surface ocean depends to a large extent on the biogeochemical controls of the seawater such as Fe-binding ligands (Gerringa et al. 2006, Baker & Croot 2010).

Assuming a homogenous distribution of ash over the 20 m mixed layer, our calculations suggest that the deposition of Kasatochi ash might have added 2.0 to 2.8 nM Fe to the ash fall region in the northeast Pacific (Table 1). Mesoscale Fe-enrichment experiments demonstrate that an increase of about 2 to 3 nM Fe is enough to trigger diatom blooms in HNLC regions (Tsuda et al. 2003, Wells 2003), suggesting that Fe input from the Kasatochi ash was sufficient to stimulate the massive phytoplankton bloom in the Gulf of Alaska (Hamme et al. 2010, Langmann et al. 2010a,b).

Our estimates of the new supply of macronutrients related to the volcanic ash fall in the region are 13 to 14 nM NO₃⁻, <0.2 nM PO₄³⁻ and 6 to 20 nM SiO₂ (Table 1). Background concentrations of macronutrients (Table 1) in the North Pacific are significantly higher compared to the estimated new supply as a re-

sult of the Kasatochi ash fall, suggesting that the impact of macronutrients released from Kasatochi ash on marine primary productivity was probably minimal. Volcanic ash releases a variety of trace metals such as Al, Cd, Co, Cu, Mn, Ni, Pb and Zn (Frogner Kockum et al. 2006, Duggen et al. 2007, Jones & Gislason 2008, Hoffmann et al. 2012). The combined effects of an array of elements released by volcanic ash can also vary depending on the phytoplankton species. A recent study suggests that the growth rate of the diatom *Thalassiosira pseudonana* was significantly increased in culture experiments due to a combination of different trace metals released from volcanic ash, rather than of Fe alone (Hoffmann et al. 2012). It is therefore possible that other trace metals besides Fe might have also influenced the phytoplankton growth in the surface ocean.

Ship-board measurements in the southern part of the bloom area showed that the phytoplankton was dominated by large diatoms (Hamme et al. 2010), similar to previous observations in the northeastern Pacific during Fe-enrichment incubation experiments (Boyd et al. 1996). Diatoms significantly contribute to the carbon uptake in the global ocean. Based on the $p\text{CO}_2$ decrease (of 25 μatm) at the Ocean Station Papa (Fig. 1), the C drawdown in August 2008 associated with the diatom bloom (extrapolated over the fertilized area) has been calculated to be ~ 6 to 17×10^{12} g C (Hamme et al. 2010). Given a typical C:Fe ratio of 10^4 for Fe uptake under 1 to 3 nM Fe concentrations (Sunda & Huntsman 1995), the C drawdown based on the new Fe-release data (Fig. 2) is 34 to 46×10^{12} g C, which is about 3 to 6 times higher than of the actual estimated C drawdown (Hamme et al. 2010). Considering the uncertainties related to the precipitation and complexation of Fe and utilization by other phytoplankton groups and bacteria, the actual C drawdown related to the North Pacific bloom (Hamme et al. 2010) could be derived by the Fe input from Kasatochi volcanic ash fallout.

Sockeye salmon population could have benefited from the 2008 Kasatochi volcanic eruption

In August-September 2008, there was an unusual increase in mesozooplankton (dominated by large copepods) in the bloom area in the northeast Pacific (Hamme et al. 2010). This increased abundance of larger copepods has been connected to the diatom bloom, which allowed the zooplankton to feed closer to the surface (Hamme et al. 2010). Juvenile sockeye salmon feed extensively on zooplankton—preferen-

tially larger zooplankton (Foerster 1968)—which were abundant in the bloom region (Hamme et al. 2010). In 2010, about 35 million sockeye returned to the Fraser River in British Columbia (Canada). This was the largest return of salmon since 1913, and about 17 times higher than the average (Larkin 2010). This enigmatic number of Fraser River sockeye returns has been linked to favorable food conditions related to the oceanic fertilization by the Kasatochi eruption, which may have increased the marine survival of juvenile sockeye that entered the ocean in summer 2008 (Parsons & Whitney 2012).

Most sockeye salmon have a 4 yr life cycle, spending 2 yr in fresh water and 2 yr in the ocean before returning to nursery rivers to spawn and die (Foerster 1968, Cass & Wood 1994). The timing of the diatom bloom matches with the ocean migration of sockeye (between July and October), considered to be one of the most critical life stages of sockeye salmon (Hartt 1980, Furnell & Brett 1986). Sockeye salmon originating from British Columbia, Washington State and southeast Alaska migrate out directly into the northeast Pacific and the Gulf of Alaska, while salmon originating from Bristol Bay migrate first across the Bering Sea to areas close to Kamchatka and south of the Aleutian Islands (Burgner 1991). A fall bloom in the Gulf of Alaska is likely to impact the British Columbia sockeye to a higher extent than Bristol Bay sockeye.

Young salmon released into the zooplankton bloom survived better compared to those entering the ocean under poor zooplankton conditions (Cross et al. 2008). Favorable food conditions in the ocean can result in increased growth rates of salmon, which can ultimately affect their overall survival (Beauchamp et al. 2007, Duff 2009). The fertilized region in the northeast Pacific is similar to the oceanic region occupied by sockeye salmon (Walter et al. 1997, Parsons & Whitney 2012). It is therefore very plausible that the diatom bloom related to the Kasatochi eruption, which covered a large part of the feeding area of sockeye salmon, stimulated the ocean food web and provided a food source for zooplankton, thus making the link to the sockeye salmon ocean survival. Coastal conditions around Vancouver Island in summer 2008 may have also played a role in the marine survival of sockeye salmon. It has been suggested that cool water temperatures around Vancouver Island in the summer of 2008 (related to a La Niña event) provided favorable conditions for estuary survival of salmon (DFO 2009).

Although the diatom bloom in late summer 2008 covered a large region in the northeast Pacific

(Fig. 1), 2010 sockeye river returns were variable along the sockeye harvest regions in the northeast Pacific. In Bristol Bay in central Alaska, the sockeye return in Nushagak River (about 11 million sockeye) was the second highest ever recorded, while sockeye returns in the Egegik River region (about 5 million sockeye) were 45% below the pre-season forecasts (Eggers & Carroll 2011). Considerable differences in terms of origin and migration movements of salmon, as well as a number of other factors including the number and size of the smolts that entered the ocean, coastal conditions during ocean entrance, and coastal survival prior to river migration might have also played an important role in the ocean survival of sockeye salmon.

Volcanic eruptions and ecosystem response in the North Pacific Ocean

Volcanic eruptions may have influenced the marine food web in the North Pacific and neighboring regions in the past (Duggen et al. 2010). Interestingly, one of the largest salmon runs in 1958 (Groot & Quinn 1987) followed the large eruption of Benzymjanny volcano in Kamchatka that started mid-November 1955 (Gorshkov 1959). It has been suggested that the ash fallout from the 1912 Katmai-Novarupta eruption in Alaska fertilized the nearby lakes (due to ash-derived phosphorus; Eicher & Rousefell 1957). However, the direct impact of the extreme ash load from this eruption was the initial mortality of pre-smolts in the local rivers caused by damage to the gills of the salmon (Eicher & Rousefell 1957, Duggen et al. 2010). Despite the smaller number of spawning fish in the rivers and lakes immediately following the Katmai-Novarupta eruption, the numbers of sockeye returning in the following 4 years were as large as pre-eruption, indicating a rapid recovery—possibly associated with favorable ocean conditions (Eicher & Rousefell 1957).

CONCLUSIONS

The role of volcanic eruptions in oceanic biogeochemical cycles is still not fully understood, but there is increasing evidence of their significant impact on marine primary production. Our study indicates that Fe released from the Kasatochi volcanic ash was sufficient to induce large-scale phytoplankton blooms, with potential implications for higher trophic levels—in this case, the sockeye salmon population. How-

ever, varying ecologic impacts of volcanic ash in fresh waters, in coastal regions and in the open ocean require more scientific attention in order to evaluate their importance for oceanic food web dynamics.

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