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## HORIZONS

# Skyfall—neglected roles of volcano ash and black carbon rich aerosols for microbial plankton in the ocean

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Mineral dust, volcano ash and soot (black carbon) are among the major solid aerosol inputs to the world ocean. They deliver elements such as C, N, P, S and bioactive trace metals in significant amounts. However, in contrast to mineral dust, the impact of volcano ash and soot on microbial plankton is poorly studied, although total deposition rates are not much lower for volcano ash than for mineral dust in certain basins and soot delivers overall more P into the ocean than mineral dust. Aging processes in the atmosphere during horizontal transport, e.g. due to exposure to UV light and acidic conditions in clouds, increase the solubility and hence bioavailability of volcano ash and soot aerosols. Current findings suggest that volcano ash and soot are a source of nutrients and/or organic carbon, and influence aggregation processes. Volcano ash seems to stimulate phytoplankton, and soot bacterioplankton; both aerosols influence microbial diversity. We argue that volcano ash and soot have a significant, but comparatively less well-studied effects on microbial plankton that should, along with mineral dust, be better implemented into concepts and studies of microbial food webs to improve the mechanistic understanding of the role and performance of autotrophic and heterotrophic microorganisms in the ocean.

**KEYWORDS:** mineral dust; volcano ash; black carbon; soot; sea spray; phytoplankton; bacteria; protists; viruses; organic matter; diversity; production

## INTRODUCTION

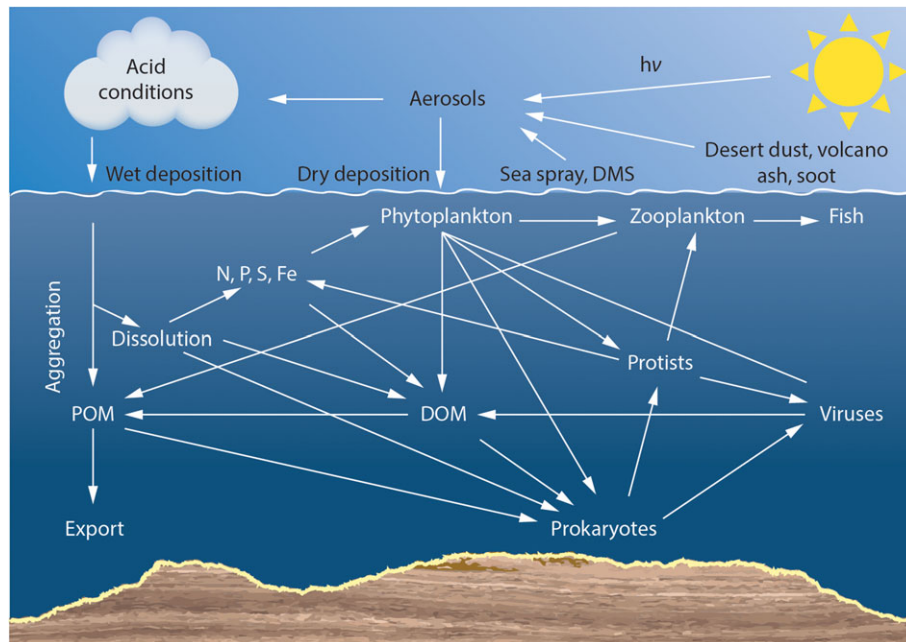
The atmosphere contains different types of aerosols, i.e. airborne solid and liquid particles (O’Dowd and De Leeuw, 2007). Aerosols are significant factors influencing climate change, e.g. due to the reduction of direct radiative forcing and by modulation of cloud properties due to their ability to act as cloud condensation nuclei (O’Dowd and De Leeuw, 2007; De Leeuw *et al.*, 2014). In the following, we focus on two major types of solid aerosols: volcano ash aerosols (VAA) and black carbon rich aerosols (soot, BCA).

Microorganisms, i.e. viruses and single-celled organisms, represent the largest marine biomass (Whitman *et al.*, 1998). They are the major biological actors involved in element cycling in the ocean (Moore *et al.*, 2013), thus being crucial players for controlling biogeochemical cycles, ecosystem functions and climate change (Kirchman, 2010). In a simplified scheme, the pelagic food web in the ocean consists of several levels. (i) The grazing food chain is the consumption of bacterial and eukaryotic phytoplankton by a series of predators including crustaceans, gelatinous plankton and fish. (ii) The microbial loop is the processing of organic matter by prokaryotes (here used in a non-phylogenetic sense for *Bacteria* and *Archaea*), which are the only major consumer of (mainly) dissolved organic matter (DOM). DOM is produced at all food web levels, e.g. by active leaching, cell death and sloppy feeding. The microbial loop is

linked to the grazing food chain by protists, which feed on prokaryotes and are consumed by larger predators. (iii) The viral shunt is the lysis of (micro)organisms by viruses, which constitutes a major pathway of DOM and small cell debris formation.

By processes such as grazing of macrozooplankton on phytoplankton, organic particles are produced. They are modified by processes of the microbial food web, sink out of surface water and transport carbon into the deep sea (biological pump). Aerosol deposition can interfere with the microbial food web and biogeochemical cycles in various ways such as due to the release of nutrients or ballasting of organic particles. For a simple scheme of aerosol deposition and some potential links to the microbial food web in the ocean, see Fig. 1.

We examine the evidence of the poorly studied role of VAA and BCA deposition for influencing microbial diversity and processes in marine systems. Some comparisons are made with the much better investigated effects of mineral dust aerosols (MDA) (for studies on the effect of MDA on microbial plankton, see e.g. Jickells *et al.*, 2005; Guieu *et al.*, 2014a; Jickells and Moore, 2015). A synthesis of findings obtained so far suggests that VAA and BCA depositions significantly influence phytoplankton and bacterioplankton; however, we also identify major knowledge gaps and potential objectives of this research.



**Fig. 1.** Schematic representation of the potential influence of aerosol deposition on the microbial food web. POM, particulate organic matter; DOM, dissolved organic matter; DMS, dimethyl sulfide.

## AEROSOLS

### Types and sources

VAA consist of fragments of pulverized rock, minerals and volcanic glass, created during volcanic eruptions. The types of minerals present in volcanic ash depend on the chemistry of the magma from which it was erupted and are dominated by silica. Volcanic eruptions occur at the edges of tectonic plate zones such as the Ring of Fire in the East Pacific Ocean or hot spots such as the Hawaii archipelago. BCA have been defined in different ways. Here, we use the term black carbon rich aerosols as a synonym for soot (products of incomplete combustion). BCA are produced during forest, savannah and grassland burning, and during combustion of fossil and bio-fuels from anthropogenic activities.

The quantity of potentially bioavailable elements in aerosols is quite variable (Table I). For example, differences of P, Fe and Si in VAA by an order of magnitude are frequently found and suggest a strong heterogeneity of the material. The estimates of the concentrations of these elements are comparatively constant for MDA. BCA mainly consist of black carbon and organic carbon right after their emission from a combustion process. During atmospheric transport, BCA usually get coated with nitrate and sulfate emitted directly as byproducts of combustion, or formed through the oxidation of SO<sub>x</sub> or NO<sub>x</sub>. Other organic species from pyrolytic carbon can condense

on BCA within a fresh combustion plume, and oxidation of anthropogenic and biogenic volatile organic carbon can later produce new carbon particles, which can be attached to the BCA mix by coagulation. Condensation, absorption and coagulation processes in the atmosphere can also lead to the transfer of organic material from combustion aerosol mixes onto VAA (and MDA).

### Transport, aging and deposition

Aerosols can be transported and spread over great distances; thus the atmosphere is generally viewed as an important transport route for many elements and compounds entering open waters (Rosman *et al.*, 1993; Migon, 2005). The worldwide distribution of some major aerosols for a specific time point is shown in Fig. 2; a detailed *ca.* 8-month time course of the development of aerosols at the global scale can be found at [http://gmao.gsfc.nasa.gov/animations/aerosols\\_geos5.mov](http://gmao.gsfc.nasa.gov/animations/aerosols_geos5.mov).

The origin of aerosols and also the origin of the air mass strongly determine the solubility of the atmospheric material. For example, Saharan MDA can be mixed during atmospheric transport with anthropogenic material such as N, P and Fe and organic material from industrial areas of North Africa (Rodríguez *et al.*, 2011) or with ship emissions (Marmer *et al.*, 2009). In addition, size-selective settling reduces the average size of the

*Table I: Representative data on the chemical composition of potentially bioreactive elements of VAA and BCA, and on deposition rates into the ocean, in comparison with MDA*

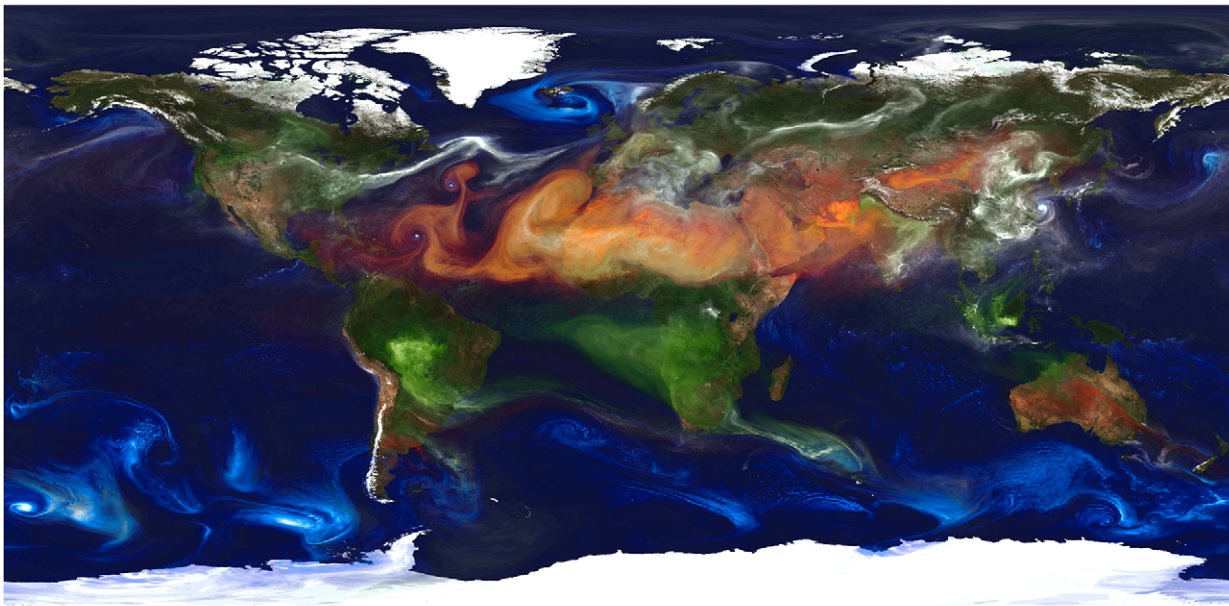
Aerosol	Chemical composition (% mass)						Deposition rate (Tg yr <sup>-1</sup> )			
	N	P	Fe	Si	Organic C	Ref	Total	Dry	Wet	Ref.
MDA	0.22	0.01–0.09	2.3–4.5	13.6	0–7 <sup>a</sup>	Guieu <i>et al.</i> (2002), Guieu <i>et al.</i> (2010), Formenti <i>et al.</i> (2008), Herut <i>et al.</i> (2005), Morales- Vaquero and Pérez- Martinez (2016)	0.44–55	0.39	0.12	Guerzoni <i>et al.</i> (1999), Ginoux <i>et al.</i> (2001), Ginoux <i>et al.</i> (2004), Jickells and Moore (2015)
VAA	<0.0038	<0.003–0.016	<0.002–0.2	<0.04–0.3	0–7 <sup>a</sup>	Chuang <i>et al.</i> (2005), Frogner <i>et al.</i> (2001), Jones and Gislason (2008), Olgun <i>et al.</i> (2013)	0.13–0.22 <sup>b</sup>	NS	NS	Olgun <i>et al.</i> (2011)
BCA	0.07–0.21	0.036–0.052	0.031–0.077	2.3–4.2	70–>90	Yamasoe <i>et al.</i> (2000)	2–48	2	10–46	Unpublished work from Guillaume <i>et al.</i> (2007); Jurado <i>et al.</i> (2008)

Data represent ranges from averages of studies or study sites and demonstrate some of the variability of estimates for the chemical composition and deposition rates of aerosols. NS, not studied.

<sup>a</sup>Amount depending mainly on association during atmospheric transport.

<sup>b</sup>Data from the Pacific only.





**Fig. 2.** Worldwide distribution of some of the major aerosols on 30 September 2006 demonstrating across-continent spread of aerosols. Note that organic matter and black carbon together with sulfates correspond to soot as defined in this study (except for volcano eruptions). The detailed time course of the development of these aerosols over the period from 17 August 2006 to 10 April 2007 can be found at [http://gmao.gsfc.nasa.gov/animations/aerosols\\_geos5.mov](http://gmao.gsfc.nasa.gov/animations/aerosols_geos5.mov). There is a persistently active volcanic emission from Mt Nyiragongo in the Democratic Republic of the Congo, Africa. For a specific large eruption from the Karthala Volcano on Grand Comore Island, Comoros, consult January 2007.

incoming aerosol and renders it more reactive to chemical processes occurring during atmospheric transport (Jickells and Moore, 2015). Similar processes can be expected for VAA and BCA. Overall, exposure to acidic conditions in clouds (leaching processes) and to solar radiation during long-range atmospheric transport increases the solubility of aerosols, and, therefore, the bioavailability of aerosols (including VAA and BCA) increases with the distance from the emissions (Desboeufs *et al.*, 2001; Jickells and Moore, 2015). The bioavailability of elements such as iron attached to VAA is still poorly known (Langmann *et al.*, 2010). Basically, standardized protocols and physico-chemical measurements such as mineralogy, pH, aerosol mass and size are still missing (Baker and Croot, 2010). BCA aging is a key topic in both climate (scattering vs. absorbing effects) and air quality sciences (change in bioavailability of toxics for humans). As BCA age in the atmosphere, the primary mix of anthropogenic pollutants is mixed with organic and inorganic matter, hence leading to brown carbon as defined by Andreae and Gelencsér (2006). Oxidation reactions involving OH and O<sub>3</sub> during atmospheric transport significantly increase water solubility and hygroscopicity of BCA (Slade *et al.*, 2015).

Although data on the atmospheric concentrations of aerosols, deposition rates into the oceans and concentrations in the water column exist, there is a poor ocean-wide coverage of such data and there are also large variations

in the literature for any given environment. Overall, global deposition rates of e.g. organic carbon or nutritive elements such as P or Fe into the ocean are difficult to quantify (O'Dowd and De Leeuw, 2007; Jurado *et al.*, 2008; Duggen *et al.*, 2010; Langmann, 2013). However, available data suggest that atmospheric deposition may supply significant loads of bioactive elements to oceanic surface waters. For example, it has been estimated that the atmospheric input of P represents up to 3.5 Tg P yr<sup>-1</sup>, including emission sources such as combustion (1.8 Tg P yr<sup>-1</sup>), mineral dust (0.93 Tg P yr<sup>-1</sup>), primary biogenic aerosols (0.58 Tg P yr<sup>-1</sup>), sea salt (0.16 Tg P yr<sup>-1</sup>) and volcanoes (0.006 Tg P yr<sup>-1</sup>) (Wang *et al.*, 2015). Cruises along the Atlantic Meridional Transect provided useful observations of the nutrient content of Saharan dust as well as of anthropogenic and biomass combustion plumes (Baker *et al.*, 2014). Specific studies estimated the deposition of nutrients from vegetation burning plumes off the coast of the Amazon basin (Yamasoe *et al.*, 2000).

The deposited aerosols can lead to quantitative disturbance in the water column, i.e. ballasting, but they can also affect the marine biogeochemistry through the solubilization of some of its components, as well as chemical species possibly adsorbed during atmospheric transport. A large number of studies have provided evidence that MDA participate to both effects (Armstrong *et al.*, 2002; Usher *et al.*, 2003). In contrast to MDA, data on

deposition rates for VAA and BCA into the global ocean are scarce or non-existent. However, millennial estimations of total VAA deposition only from the Pacific are not much lower than the estimated MDA deposition into the global ocean (Table I). BCA deposition rates are significantly higher (Jurado *et al.*, 2008; unpublished work from Guillaume *et al.*, 2007). Consequently, the high content of bioactive species in BCA, such as N from anthropogenic sources (Baker *et al.*, 2014), may well play a significant role for water column biogeochemistry. Overall, deposition rates for VAA and BCA are much higher for wet than for dry deposition (Table I). Also, deposition differs between ocean basins (e.g. Fig. 2) and on temporal scales, i.e. the deposition of VAA is more episodic than that of BCA.

### Climate effects

It is well established that volcano eruptions affect the heat budget by potentially antagonistic effects, i.e. increasing albedo on the one hand (negative radiation forcing by reduced reflectance) and by providing nuclei for cloud formation on the other hand (Rosenfeld, 2000; Ramanathan *et al.*, 2001). Organic and black carbon emissions occur in large amounts in the fast developing regions of Asia, as well as South America, sub-Saharan Africa and South Asia, where extensive biomass and fossil fuel burning occurs seasonally (Guinot *et al.*, 2007; Niu *et al.*, 2015). BCA is considered, in addition to vapor, CO<sub>2</sub> and methane, as an important atmosphere component driving radiative forcing and thus climate change (Jacobson, 2002; Forster *et al.*, 2007). The net outcome of the potentially temperature-reducing albedo effects of BCA and potentially temperature-increasing greenhouse effects is likely an increase of temperature (Jacobson, 2002; Ramanathan and Carmichael, 2008). In an investigation examining temporal trends from 1979 to 2013, the length of the fire weather season increased by ~20%, the global burnable area affected by long fire weather seasons doubled and the global frequency of long fire weather seasons increased by 50% during the second half of the study period (Jolly *et al.*, 2015). Such events including land-use changes are likely due to enhanced global temperatures and could increase the rates of BCA deposited into the ocean.

## AEROSOL–MICROBE INTERACTIONS: KNOWN AND POTENTIAL ROLES

In the following, some types of aerosol–microbe interactions and intertwined roles are discussed, and these roles

are organized into effects in the atmosphere such as dry and wet deposition and horizontal transport, and into effects in the water column such as nutrient enrichment, organic matter aggregation, microbial production/bioavailability and biodiversity. In Table II, studies on VAA and BCA effects in the water column are summarized.

### Origin of aerosols and atmospheric transport

There is a large physical and chemical variability of aerosols (e.g. Table I) depending e.g. on the origin and aging during transport in the atmosphere thus, potentially resulting in different responses of microbial plankton. For example, in experiments bacterial production and respiration were enhanced more with BCA collected *in situ* than with BCA reference material (Mari *et al.*, 2014). Differential responses of phytoplankton have also been reported for VAA (Mélanon *et al.*, 2014). Exposure of BCA reference material to solar radiation prior to incubation stimulated the production of bacterioplankton compared to unexposed BCA, probably due to changes of organic matter adsorption and/or bioreactivity (Malits *et al.*, 2015). Exposure of aerosols to the acidic conditions of clouds will likely also affect their chemical composition and reactivity (Desboeufs *et al.*, 2001), and consequently their impact on microorganisms. Also, whether material is deposited by dry (rather continuous but moderate) or wet deposition (rather episodic but massive) will have a significant influence on microbial plankton as demonstrated for MDA (e.g. Guieu *et al.*, 2014a). Finally, the interactions between aerosols and the surface microlayer, i.e. the top layer of the ocean as a site of first contact of aerosols with the ocean, will be crucial for determining the fate of aerosols and their influence on microbial activity and diversity.

Microorganisms can be transported in the material from which aerosols originate, and in the atmosphere air-borne microorganisms (which can also originate from sea spray) can get attached to aerosols. Upon deposition into the ocean, these attached microorganisms can contribute to the native microbial food web. The effect remains unstudied for VAA and BCA.

In this context, it is noteworthy to mention another type of important aerosols, sea spray, which is produced directly from the surface microlayer and water below. This ‘skin’ of the ocean is enriched in DOM including dimethyl sulfide (DMS), debris, viruses and microbes compared to underlying water, and variable in composition (Cunliffe *et al.*, 2013). Due to evaporation, winds and waves, the seawater droplets and their content material are transferred from the

Table II: Potential effects of VAA and BCA deposition on biogeochemical processes and microbial plankton in some in situ and experimental studies

Aerosol/environment	Study type	Nutrients	Aggregation/export	Phytoplankton	Bacteria	Viruses	Ref.
VAA							
Various	<i>In situ</i> , experimental	+Fe, +NH <sub>3</sub>	NS	+Chl <i>a</i>	NS	NS	Duggen <i>et al.</i> (2007)
NE Pacific	<i>In situ</i>	+Fe	NS	cDiv, +Chl <i>a</i>	NS	NS	Hamme <i>et al.</i> (2010)
NE Pacific	Experimental		NS	+Chl <i>a</i>	NS	NS	Langmann <i>et al.</i> (2010)
Cultures	Experimental	Various	NS	+ <i>Thalassiosira pseudonana</i> , – <i>Emiliania huxleyi</i>	NS	NS	Hoffmann <i>et al.</i> (2012)
NE Pacific	Experimental	+Fe	+E	+Chl <i>a</i> , +PP	NS	NS	Achterberg <i>et al.</i> (2013)
North Atlantic	<i>In situ</i> , experimental	+Fe	NS	cDiv, +Chl <i>a</i>	NS	NS	Mélançon <i>et al.</i> (2014)
Southern Ocean, South Atlantic	Experimental	+Fe, +Mn	NS	cDiv, +Chl <i>a</i> , +APE	NS	NS	Browning <i>et al.</i> (2014)
BCA							
Med Sea	Experimental	NS	+A	NS	cDiv, –12% BA <sub>t</sub> , +20% BA <sub>t</sub> , –(28–61)% BA <sub>f</sub> +60% BP	cDiv, –(41–53)% VA <sub>t</sub> , –(79–83)% VA <sub>f</sub>	Cattaneo <i>et al.</i> (2010), Weinbauer <i>et al.</i> (2012)
Med Sea	<i>In situ</i> (forest fire)	+1.4–4xNO <sub>3</sub> , PO <sub>4</sub>	NS	±Chl <i>a</i> , ±PP		NS	Bonilla-Findji <i>et al.</i> (2010)
Off New Caledonia	<i>In situ</i> (power plant)	NS	+(30–40)xPVC, +5.5xSPM, +A	±Chl <i>a</i>	–23+BA <sub>f</sub> , +3xBP <sub>t</sub> , +2xBP <sub>a</sub> , +30% BR <sub>t</sub>	–33% VA <sub>f</sub>	Mari <i>et al.</i> (2014)
North Sea	Experimental	NS	NS	±PP	–11% BA <sub>f</sub> , +8.2xBP, +<4xBR	–15% VA <sub>f</sub>	Mari <i>et al.</i> (2014)
	Experimental	+(45–60)% PO <sub>4</sub> , +(5.3–6.6)xNH <sub>4</sub>	NS	NS	±BA <sub>f</sub> , +(43–76)% BP <sub>t</sub>	–(11–43)% VA <sub>f</sub> , –(64–91)% VP, –(50–92)% FIC	Malits <i>et al.</i> (2015)

Depending on data presentation in the literature, stimulation (+) and repression (–) by aerosols deposition/addition are given as averages or maximum impact in percent (per event or experiment) or only qualitatively. ±, no detectable effect; A, aggregation; APE, apparent photochemical efficiency; BA, bacterial abundance; BCA, black carbon rich aerosols; BP, bacterial production; BR, bacterial respiration; cDiv, change in diversity; Chl *a*, Chlorophyll *a*; E, export; FIC, fraction of infected cells; NS, not studied (in the sense of quantitative data); PP, primary production; PVC, particle volume concentration; SPM, suspended particulate matter; VAA, volcano ash aerosols; VA, viral abundance; VP, viral production; a, attached; f, free-living; t, total (i.e. attached + free-living); x, x-fold.

surface ocean into the atmosphere (Kuznetsova *et al.*, 2005; Prather *et al.*, 2013; Lee *et al.*, 2015; Wang *et al.*, 2015). Following potential changes in composition and structure during exposure in the atmosphere, which probably increase solubility and bioavailability as for other aerosols (see above), the spray will be deposited again into the ocean and potentially influence microbial plankton. To the best of our knowledge, no studies have specifically addressed this issue of spray–microbe interactions for the ocean.

### Ocean acidification

Addition of BCA reference and natural material to seawater can decrease the pH and thus BCA deposition constitutes a non- $p\text{CO}_2$ -based mechanism of ocean acidification (Weinbauer *et al.*, 2012). Simulating a typical deposition event in the middle of the coral reef lagoon of Noumea (New Caledonia), a  $1\text{ mg L}^{-1}$  addition of natural BCA material reduced the pH by more than 0.1 units. This BCA-based acidification occurs at a level that can affect organic matter aggregation, microbial activity and diversity (Liu *et al.*, 2010; Mari *et al.*, 2014). While deposition of anthropogenic atmospheric nitrogen and sulfur is likely to have only a small contribution to global ocean acidification, it is potentially important regionally, such as in specific coastal regions (Doney *et al.*, 2007).

### Sources of toxic compounds

VAA contain toxic metals and BCA contain toxic metals and toxic organic compounds (Jones and Gislason, 2008; Fang *et al.*, 2015). Transitory toxic effects for phytoplankton have been shown for VAA (Duggen *et al.*, 2010). Toxic effects of copper for phytoplankton growth and taxonomic composition have been demonstrated recently for (anthropogenic) aerosols (Paytan *et al.*, 2009; Jordi *et al.*, 2012).

### Nutrient enrichment

Since iron is associated with specific aerosols, aerosol deposition is linked to the iron hypothesis, i.e. the idea of Martin (1990) that in oceanic high-nutrient low-chlorophyll (HNLC) areas phytoplankton growth is limited by iron. *In situ* observations and fertilization studies have resulted in a large body of evidence that some oceanic areas and many microbial processes are iron-limited (Boyd *et al.*, 2007; Smetacek and Naqvi, 2008).

MDA contain significant amounts of bioavailable iron and, it is assumed, at least for offshore environments, that bioavailable iron originates from MDA. However, recent evidence such as from ocean drilling, geochemical and biological experiments, and satellite techniques, suggests that the deposition of VAA is an underestimated source

for iron in the surface ocean. Release rates of iron are possibly of similar importance compared to aeolian dust (Duggen *et al.*, 2010) and total deposition rates are roughly similar for MDA and VAA (Langmann, 2013) (Table I).

VAA deposition from volcanic eruptions can induce anomalously large phytoplankton blooms, and ship-based experiments performed in parallel to eruption events with collected VAA frequently showed an increased dominance by diatoms (Hamme *et al.*, 2010; Browning *et al.*, 2014). Overall, data suggest that VAA deposition can temporarily relieve iron limitation for phytoplankton production in HNLC areas (Hamme *et al.*, 2010; Achterberg *et al.*, 2013), although VAA can also be toxic for some phytoplankton species (Hoffmann *et al.*, 2012). There is also evidence that manganese could be a limiting factor or a co-limiting factor to iron (Browning *et al.*, 2014) and that  $\text{NH}_3$  deposition by VAA could be important in some areas (Duggen *et al.*, 2007). VAA contain phosphorus, which can be released in significant amounts into seawater (Olgun *et al.*, 2013). Thus, there is the possibility that VAA deposition could relieve P-limitation of phytoplankton and bacterial production in P-limited systems, such as the Mediterranean Sea (Olgun *et al.*, 2011).

Natural soot and black carbon reference material contain nutrients such as  $\text{NH}_4$ ,  $\text{NO}_3$  and  $\text{PO}_4$  (Yamasoe *et al.*, 2000; Weinbauer *et al.*, 2012). For example, BCA is the largest source of P in aerosols (Wang *et al.*, 2015); release of  $\text{NH}_3$  and  $\text{NH}_4$  has also been demonstrated (Table II; Yamasoe *et al.*, 2000). Thus, BCA deposition could partially relieve nutrient limitation. During a period of increased forest fires and BCA deposition along the Mediterranean coast of France in 2003,  $\text{PO}_4$  and  $\text{NO}_3$  concentrations were elevated by 1.4 to 4-fold, bacterial production by 60% and growth efficiency by 2.9-fold, whereas the typical accumulation of dissolved organic carbon (DOC) did not occur. The deposition of inorganic phosphorus could have partially relieved P-limitation (and potentially co-limitation by N) of bacterioplankton and thus, resulted in the use of DOC (Bonilla-Findji *et al.*, 2010).

The majority of the studies on the biological effects of VAA deposition have addressed the relief of nutrient (mainly Fe) limitation for phytoplankton growth. Almost nothing is known for bacterioplankton. Also, the role of VAA and BCA deposition for relieving the potential limitation of microbial growth by other nutrients or elements such as N, P, S or Mn remains poorly known.

### Sources of bioavailable organic matter

MDA deposition is a source of organic carbon and it has been shown that DOM can stimulate bacterial



abundance and respiration in natural conditions and in experiments (Pulido-Villena *et al.*, 2008). Whether or not VAA deposition also transports organic matter (e.g. adsorbed during atmospheric transport) to the ocean remains unknown. BCA deliver organic matter to the ocean; however, it is not known whether part of this typically rather (semi)refractory core material is easily bioavailable. Organic material adsorbed to BCA during atmospheric transport is potentially bioactive (Baker *et al.*, 2014).

### Particle-attachment and aggregation

Preliminary data suggest that organic matter such as transparent exopolymeric particles (TEP) and microorganisms can become rapidly associated to VAA upon deposition into the ocean (Weinbauer, unpublished results). More information is available for BCA. For example, the capacity of black carbon and similar materials for organic matter adsorption is well known ('charcoal effect'; Weinbauer *et al.*, 2012). In experiments, where black carbon reference material was added to seawater, the formation of TEP was stimulated (Weinbauer *et al.*, 2012; Mari *et al.*, 2014). Also, *in situ* data from a BCA deposition event suggest rapid aggregation of organic matter (Mari *et al.*, 2014). Associations between bacteria and black carbon reference material present a continuum from small soot colloids attached to bacteria, to bacteria completely entrapped in a soot matrix (Cattaneo *et al.*, 2010; Malits *et al.*, 2015). Experimental work has shown that addition of soot reference material to seawater resulted in immediate adsorption of 10–25% of bacterial and viral abundances (Cattaneo *et al.*, 2010; Weinbauer *et al.*, 2012), and such an adsorption has also been observed *in situ* (Mari *et al.*, 2014).

It is known that bacterial activity is often higher on organic particles than in surrounding water, e.g. due to adsorption or aggregation of organic matter, thus concentrating organic matter (Simon *et al.*, 2002). This could create new hot spots of microbial activity and organic matter transformation (Azam and Malfatti, 2007). While the abundance of the total and the free-living bacterial community was typically not affected or reduced by BCA addition (experimental and *in situ*), bacterial production and respiration were typically stimulated (Table II). For example, during an *in situ* study offshore a barrier reef, attached bacterial production doubled, total bacterial production tripled and bacterial respiration increased by 30% after BCA deposition (Mari *et al.*, 2014). Thus, aggregation due to BCA could enhance bacterial production. Concentrating organic matter due to adsorption onto VAA could also stimulate

bacterial production; however, this remains to be investigated.

### Metabolic balance

The stimulation of massive phytoplankton blooms by VAA deposition events (Table II) could suggest that the production (P) to respiration (R) ratio is shifted towards autotrophy ( $P:R > 1$ ). However, quantitative data on heterotrophic production during or following such blooms are not available. Current knowledge suggests that BCA deposition stimulates bacterial production, but not primary production (Table II). Therefore, the findings suggest a shift toward autotrophy by VAA ( $>P:R$ ) and shifts toward heterotrophy by BCA ( $<P:R$ ).

### Microbial community structure and diversity

*In situ* and experimental data on VAA deposition suggest changes in phytoplankton diversity, often favoring a dominance of diatoms (Table II). In experiments with Eyjafjallajökull volcano ash in the Western Pacific and the Mediterranean Sea, changes in bacterial diversity were observed (R. Zhang, personal communication; Weinbauer, unpublished results).

Experiments with BCA reference material indicate that soot can induce changes of community composition of free-living bacteria. The two phylotypes only detected in the treatment with BCA reference material corresponded to the genus *Glaciecola* (Cattaneo *et al.*, 2010). Also, a flow cytometer analysis showed that the addition of this material resulted in a change of viral groups and, thus, diversity of the viroplankton (Weinbauer *et al.*, 2012).

The few studies performed suggest a strong potential for aerosol deposition to cause shifts in biodiversity. The matrix and material of aerosols could for example provide niches for microorganisms, hence rather sustaining than repressing diversity. In addition, microorganisms attached to aerosols (from the original source or during transport; see also the section on atmospheric transport) could be a source of local and regional biodiversity upon deposition into the ocean.

### Predatory losses

Almost nothing is known about the influence of aerosol deposition on predators and the predatory losses of microbial plankton (mainly viral lysis and protistan grazing). One study suggests that attachment to BCA reduces viral infection and production (by *ca.* 50–90%; Table II) by inactivating viruses or preventing infection of bacteria (Malits *et al.*, 2015). Such a diminution of viral infection

could be responsible for the increase bacterial activity observed both *in situ* (Mari *et al.*, 2014) and in laboratory experiments (Cattaneo *et al.*, 2010; Malits *et al.*, 2015). Overall, these mechanisms are crucial to understanding the flow of carbon and nutrients, food web structure and diversity of microbial plankton; however, they remain poorly studied for BCA and unstudied for VAA.

### Some other effects

Owing to their high density, aerosols deposited into the ocean and aerosols attached to organic particles (ballasting) can sink out of the euphotic zone and transport organic matter and attached microorganisms (either deposited along with aerosols or adsorbed in the water column after deposition) can be transported into the deep sea. As discussed above, aerosol deposition could change the patterns of production and organic matter use and thus impact the formation of organic aggregates, e.g. during and after phytoplankton blooms. This could affect the export of organic matter (Duggen *et al.*, 2010; Mari *et al.*, 2014). An export into the interior of the ocean represents an aerosol link to the biological pump as e.g. demonstrated for MDA (Ternon *et al.*, 2010). Processes, such as the potential effect of MDA on nitrogen fixation thus possibly forcing of the system toward P-limitation (Guieu *et al.*, 2014a), could also be initiated by VAA and BCA. For firmer conclusions on the effect of aerosol deposition on export, larger and more detailed data sets are needed.

### Other aerosols

Anthropogenic material, such as metals, organic compounds, nano-particles and large plastic particles (Thompson *et al.*, 2009) and toxic organic material, is deposited in large quantities. Sea-spray is a significant, marine-borne aerosol that can also interact with MDA, VAA and BCA (Fig. 1). However, the effects of these aerosols on microbial plankton are poorly studied and represent an additional future avenue for the study of aerosol–microbe interactions.

## CONCLUSIONS

The data presented suggest that Fe release could be roughly comparable between VAA and MDA, that total deposition rate is not much lower for VAA than for MD and that more P is deposited into the ocean by combustion than by MDA. However, deposition does not only vary between ocean basins (see e.g. Fig. 2), but also on temporal scales, e.g. VAA deposition is more episodic

than MDA deposition. Also, we demonstrate that VAA and BCA can influence microbial diversity and processes; overall VAA seem to stimulate phytoplankton production and BCA seem to stimulate bacterial production. In addition, many processes are poorly or not at all studied, such as the effect of atmospheric transport on the bioavailability of associated material and the effect of VAA on bacterial production. Hence, deposition of the ‘neglected’ aerosols should be implemented into the concepts of microbial food webs to improve the mechanistic understanding of the multifaceted role and performance of autotrophic and heterotrophic microorganisms in the oceans.

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