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TOPICAL REVIEW

# Aerosols in atmospheric chemistry and biogeochemical cycles of nutrients

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## Abstract

Atmospheric aerosols have complex and variable compositions and properties. While scientific interest is centered on the health and climatic effects of atmospheric aerosols, insufficient attention is given to their involvement in multiphase chemistry that alters their contribution as carriers of nutrients in ecosystems. However, there is experimental proof that the nutrient equilibria of both land and marine ecosystems have been disturbed during the Anthropocene period.

This review study first summarizes our current understanding of aerosol chemical processing in the atmosphere as relevant to biogeochemical cycles. Then it binds together results of recent modeling studies based on laboratory and field experiments, focusing on the organic and dust components of aerosols that account for multiphase chemistry, aerosol ageing in the atmosphere, nutrient (N, P, Fe) emissions, atmospheric transport, transformation and deposition. The human-driven contribution to atmospheric deposition of these nutrients, derived by global simulations using past and future anthropogenic emissions of pollutants, is put into perspective with regard to potential changes in nutrient limitations and biodiversity. Atmospheric deposition of nutrients has been suggested to result in human-induced ecosystem limitations with regard to specific nutrients. Such modifications favor the development of certain species against others and affect the overall functioning of ecosystems. Organic forms of nutrients are found to contribute to the atmospheric deposition of the nutrients N, P and Fe by 20%–40%, 35%–45% and 7%–18%, respectively. These have the potential to be key components of the biogeochemical cycles since there is initial proof of their bioavailability to ecosystems. Bioaerosols have been found to make a significant contribution to atmospheric sources of N and P, indicating potentially significant interactions between terrestrial and marine ecosystems. These results deserve further experimental and modeling studies to reduce uncertainties and understand the feedbacks induced by atmospheric deposition of nutrients to ecosystems.

## 1. Background

Atmospheric aerosols are liquid or solid particles suspended in the atmosphere; they range from about 3 nm to 100 $\mu$m in diameter and they have different shapes, chemical compositions and hygroscopic and optical properties (Seinfeld and Pandis 2006, Pöschl and Shiraiwa 2015). The properties of aerosols depend on their source, transport and transformation in the atmosphere, and they are modified by the so-called atmospheric ageing that includes chemical and physical processing in the atmosphere (Kanakidou *et al* 2005, Boucher 2015). Aerosols affect human health by inhalation and subsequent production of reactive oxidative stress (Pöschl and Shiraiwa 2015, Lelieveld *et al* 2015), and long-term exposure can lead to lung cancer and cardiopulmonary disease (Pope III *et al* 2002, Pope III and Dockery 2013). It is currently estimated that each year around 4.5 million premature deaths occur due to air pollution, with the most affected

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countries being China, India and Russia; most of these effects are linked to atmospheric aerosols (Lelieveld and Pöschl 2017). Aerosols also affect climate directly since they interact with radiation by scattering or absorbing light (Boucher 2015, Carslaw *et al* 2010), although quantification of the impact of absorbing aerosols such as black and brown carbon remains challenging (Lack *et al* 2012, Zhang *et al* 2017). The indirect effect on climate is associated with so-called aerosol–cloud interactions that alter the atmospheric water cycle (Ramanathan *et al* 2001, Stevens and Feingold 2009, Christensen *et al* 2016). Less attention has been given to the effect of aerosols on climate associated with the modification of ecosystem functioning (e.g. Arneth *et al* 2010), especially via atmospheric deposition of nutrients carried by aerosols (e.g. Mahowald *et al* 2008, 2009, 2017, Aumont and Bopp 2006, Aumont *et al* 2008) and the carbon sequestration sink (e.g Guieu *et al* 2014a, 2014b, Pitta *et al* 2017, Christodoulaki *et al* 2016, Duce *et al* 2008). Atmospheric $O_2$ and biomass production, both required to sustain life on Earth, are controlled by the photosynthetic activity of terrestrial and marine ecosystems (Pepper *et al* 2015), which in turn is limited (Moore *et al* 2013) by the availability of trace elements needed for synthesis of amino acids, nucleic acids and proteins, the building blocks of life. Aerosols carry such trace elements and provide them to ecosystems via atmospheric deposition (Mahowald *et al* 2017). During atmospheric transport, the bioavailability of this atmospheric pool of trace elements in aerosols increases (Baker *et al* 2006b) and the amounts deposited affect sequestration of atmospheric carbon (Jickells *et al* 2017) into terrestrial and marine environments, and the levels of $O_2$ in subsurface oceans (Ito *et al* 2016)—with profound implications for climate, fisheries, marine life and biodiversity (Paytan *et al* 2009).

In the atmosphere, aerosols, aerosol-associated water and cloud water also serve as media for multiphase chemistry, the main difference among them being the percentage water content and thus the level of dissolution of various compounds in water, which strongly affects pH levels. Cloud water chemistry has attracted attention for more than two decades (e.g. Erel *et al* 1993, Herrmann *et al* 2000, Warneck 2005 and references therein), in particular with regard to the oxidation of organics in the atmosphere. Recently, multiphase chemistry (in aerosol, cloud and fog waters) has been recognized as an important driver of atmospheric oxidant levels, with redox reactions and organic chemistry being involved (e.g. Lim *et al* 2010, Myriokefalitakis *et al* 2011, Mao *et al* 2013), and it affects the composition and properties of aerosols (e.g. Rudich 2003, Carlton *et al* 2007, 2008, Ervens and Volkamer 2010, Carlton and Turpin 2013, Ervens 2015, Myriokefalitakis *et al* 2015, 2016). Multiphase chemistry also contributes to the fixation of nutrients like N onto aerosols, and to the conversion of insoluble forms of trace elements like Fe and P into soluble, and thus readily bioavailable, material for uptake by ecosystems. These changes affect the nutrients carried by aerosols to ecosystems and remain understudied.

The present review aims to fill this gap by integrating knowledge about the impact of multiphase chemistry on atmospheric water acidity, composition and the solubility of nutrients that determines their bioavailability, focusing on the biogeochemical cycles of N, P and Fe, including their organic fractions and impact on marine ecosystems (figure 1). This study builds upon earlier review papers on organic aerosol formation, properties and impacts on the climate system (Kanakidou *et al* 2005, Hallquist *et al* 2009), on fog and cloud chemistry, hereafter both referred to by the term cloud chemistry (Ervens 2015), and aerosol water (McNeill 2015), on multiphase chemistry at the biosphere–atmosphere interface (Pöschl and Shiraiwa 2015), and on aerosol deposition and its impact on ecosystems (Mahowald *et al* 2017). It integrates recent global modeling studies of the atmospheric deposition of nutrients (N, P, Fe) that, based on laboratory and field experiments, account for the changes in biogeochemical cycles induced by chemical formation and processing of aerosols in the atmosphere. It also summarizes the findings on the impact of atmospheric deposition of these nutrients on ecosystems. Focus is put on the organic fraction of nutrients and the multiphase chemistry-driven solubilization of trace elements, like Fe and P, to their readily bioavailable form, on dust aerosols. Simulations using past and future anthropogenic emissions of pollutants show the importance of human-induced emissions on nutrient atmospheric deposition and biogeochemical cycles. Uncertainties and implications are also presented.

## 2. Nutrients in the atmosphere

Natural and anthropogenic aerosol sources are very diverse (figure 1). Natural sources include emissions from soils, particularly in arid areas, the sea surface, volcanoes, terrestrial vegetation and wild fires; anthropogenic sources are associated with various combustion processes, including energy production, the residential and transport sectors, solvent use, agriculture and industrial activities (Lamarque *et al* 2010, Carslaw *et al* 2010, Kanakidou *et al* 2012, Boucher 2015, Fröhlich-Nowoisky *et al* 2016).

Humans have significantly modified the composition of atmospheric aerosols due to direct emissions of various aerosol components (carbonaceous aerosols that include black, brown and organic carbon) or their precursor molecules, like sulfur dioxide, nitrogen oxides and volatile organic compounds (e.g. Galloway *et al* 2004, Lamarque *et al* 2010, Kanakidou *et al* 2005, Fuzzi *et al* 2006, Goldstein and Galbally 2007, Hallquist *et al* 2009).

However, both natural and anthropogenic sources also emit into the atmosphere various other trace

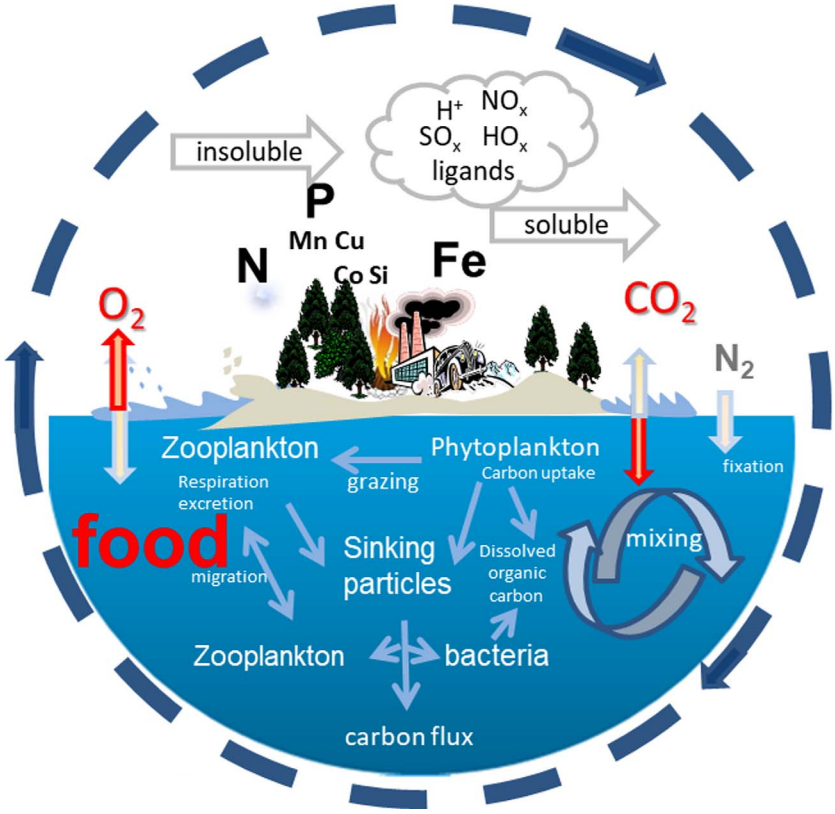


**Figure 1.** Terrestrial vegetation and marine phytoplankton are responsible for producing the $O_2$ in the atmosphere of our planet and the majority of the removal of $CO_2$ from the atmosphere. Photosynthesis requires nutrients that can be supplied to ecosystems by atmospheric deposition of trace elements, carried by aerosols, which can be considered as a major source of nutrients for ecosystems. Multiphase chemistry in the atmosphere converts insoluble trace elements to soluble (bioavailable) nutrients. This chemical process has been neglected so far in most global modeling of biogeochemical cycles. The feedback of aerosols on climate via atmospheric deposition and the impact of the biogeochemical cycling of nutrients have been neglected in climate modeling until now.

elements attached to the aerosol phase, such as P (Anderson *et al* 2010, Paytan and McLaughlin 2007) and metals, including Fe, Cu, Cd, Co, Ni, Hg, Zn, Pb and As, among many others (Paytan and McLaughlin 2007, Rauch and Pacyna 2009). Metals can also be present in the aerosol phase as free ions or complexes in inorganic or organic forms. N, P and many metals (e.g. Fe, Cu, Ni, Co, Cd, Zn) are essential micronutrients for marine phytoplankton, but at high levels they can be toxic (Paytan *et al* 2009). N, P and Fe are known to control primary productivity in vast areas of the open ocean (Moore *et al* 2013, Okin *et al* 2011).

### 2.1. Organics as carriers of nutrients

Organics are key players in biosphere–atmosphere–climate interactions (e.g. Kulmala *et al* 2004) and their role as carriers of nutrients has only recently been recognized (Anderson *et al* 2010, Cornell 2011, Kanakidou *et al* 2012). They have a significant human-driven component due to primary anthropogenic emissions (Lamarque *et al* 2010), (Hoesly *et al* 2018) or the interaction of natural emissions with pollution (Kanakidou *et al* 2000, 2012 Spracklen *et al* 2011). This organic pool in the atmosphere has a variable content of C, H, O, N and other elements depending on the origin and the history of organics in the atmosphere, especially between anthropogenic (fossil) and biogenic sources. In the early 1950s van Krevelen introduced a method for studying the H:C content of organic compounds as a function of their O:C content (van Krevelen 1950) in order to track the origin and maturity of kerogen and petroleum. With the increasing power of analytical techniques (Aiken *et al* 2008) these plots, now known as van Krevelen diagrams, started to be used to understand the origin and properties of organic aerosols in the atmosphere in order to simplify the representation of a very complex pool of compounds (Heald *et al* 2010). Recently, van Krevelen diagrams have been also extended to include elements such as N (Altieri *et al* 2012). Element ratios have also been used to understand the organic N and organic P atmospheric cycles based on the relatively better understood organic C cycle (Kanakidou *et al* 2012, 2016, Myriokefalitakis *et al* 2016).

During the last decade attention has been paid to biological material that is widely found as part of the organic aerosols directly emitted by vegetation (Jaenicke 2005), as well as to the amounts of organics present in soils and potentially carried by soil dust aerosols (e.g. Schlesinger 1977, Kanakidou *et al* 2012 and references therein), further discussed in section 3.1. Remarkably, organic aerosols are found to

be more abundant at several locations in the atmosphere (Jimenez *et al* 2009) compared with the sulfate aerosols (Tsigaridis and Kanakidou 2007) that have been mitigated the past decades (Lamarque *et al* 2010, Hoesly *et al* 2018). Following this reduction in sulfate, sulfate-associated organics in the aerosol phase have decreased, as well as aerosol hydroscopicity and thus the aerosol-associated water over polluted regions in the USA (Attwood *et al* 2014, Boulanger 2015), with potential implications for multiphase chemistry and aerosol acidity.

### 2.2. Primary aerosol sources

Aerosols are present in the atmosphere in different sizes, ranging from submicron to supermicron aerosols, with diameters smaller and larger than 1 $\mu$m, respectively. Until recently, most of the modeling studies of aerosols have considered the $PM_{10}$ aerosol fraction, i.e. those with diameters smaller than 10 $\mu$m (Textor *et al* 2006), and have neglected the larger supercoarse mode. Therefore, in the following discussion we neglect the supercoarse aerosols, except when specifically mentioned.

#### *2.2.1. Dust*

Dust and sea spray are the largest components of atmospheric aerosols, with mass emissions to the atmosphere two to three orders of magnitude higher (of one to several thousand Tg $yr^{-1}$) than other aerosol components (Boucher 2015). Large uncertainties exist in their fluxes, some of which is due to the contribution of the different size distributions of aerosols taken into consideration in individual studies. This is also reflected in model estimates of dust fluxes, where differences of almost an order of magnitude in dust emissions are calculated between models with a wide variety of assumptions on dust size distribution (Textor *et al* 2006). Indeed, dust particles have diameters spanning from 100 nm to a few tens of micrometers. Escribano *et al* (2017), in a regional inverse modeling study, estimated that mineral dust emissions over northern Africa and the Arabian Peninsula ranged between 2550 and 4210 Tg $yr^{-1}$, accounting for supercoarse particles with diameters smaller than 30 $\mu$m; this estimate is reduced by a factor of four to five when only diameters smaller than 6 $\mu$m are considered. The fine dust particles can be transported for long distances after being lifted from the surface, while the larger dust particles are quickly deposited by gravitational settling, therefore affecting only local ecosystems (Boucher 2015, Tipping *et al* 2014).

Globally, dust is a major source of trace elements contained in minerals (Claquin *et al* 1999, Nickovic *et al* 2012, Usher *et al* 2003), in particular Fe (Jickells *et al* 2005, Mahowald *et al* 2009) and P (Mahowald *et al* 2008, Myriokefalitakis *et al* 2016). The total Fe content of dust (mean mass) is about 3.5%. This varies with dust mineralogy (Claquin *et al* 1999, Journet *et al* 2008, 2014, Shi *et al* 2012, Perlwitz *et al* 2015), and even for specific minerals it varies significantly, for instance between 0.24% and 0.7% for kaolinite and between 55% and 77.4% for hematite (Nickovic *et al* 2013, Journet *et al* 2008). Note that these values are associated with large uncertainty. Estimated ranges for total Fe and total P dust emissions, neglecting supercoarse particles, range from about 35 to as high as 115 Tg Fe $yr^{-1}$ (Myriokefalitakis *et al* 2015, Ito and Kok 2017) and from 1.1 to 3.8 Tg P $yr^{-1}$ (Myriokefalitakis *et al* 2016, Brahney *et al* 2015, Graham and Duce 1979). Observations have shown that freshly emitted dust aerosols contain significant amounts of insoluble trace elements, in particular Fe and P, but only a very small fraction of these are in a readily bioavailable soluble form (Tagliabue *et al* 2017).

The soluble Fe fraction is <0.5% of total Fe mineral dust emissions (Fung *et al* 2000, Hand *et al* 2004, Sedwick *et al* 2007) Atmospheric chemical processing, transport and removal drastically alter Fe solubility in airborne dust (Baker and Jickells 2006). Observations suggest solubilities of below 1% for fresh atmospheric dust aerosols (e.g. Chuang *et al* 2005, Baker *et al* 2006a, Baker *et al* 2013; see also the comprehensive review by Sholkovitz *et al* (2012)) while solubilities in the range of 2.3%–67% have been observed in atmospheric processed aerosols, based on observations during oceanographic cruises (e.g. Baker *et al* 2006b, Furutani *et al* 2010), and high solubilities of 82 ± 18% have been measured in precipitation in the Southern Ocean (Heimburger *et al* 2013). Theodosi *et al* (2010) observations of Fe solubility in rainwater in the eastern Mediterranean for over 2 years have shown a pH-driven Fe solubility, with the lowest solubility of 0.5% associated with Saharan dust episodes (rainwater pH = 8) and the highest (27.5%) with polluted air masses. Overall, the observed atmospheric Fe solubility for various types of aerosols spans over more than three orders of magnitude from 0.01% to 80% (Sholkovitz *et al* 2012).

#### *2.2.2. Sea spray*

Sea spray aerosol formation is mainly driven by wind, and occurs by the ejection of surface seawater to the atmosphere in the form of droplets during the bursting of bubbles in seawater. Evaporation of part of the water from the ejected droplets leads to the formation of aerosols spanning sizes from fine to supercoarse (Lewis and Schwartz 2004). Therefore, sea spray aerosol composition reflects that of surface seawater and, in particular, of the surface microlayer, which is enriched in several substances, primarily organics, compared with the underlying seawater (e.g. Duce and Quinn 1972, Aller *et al* 2005, Ebling and Landing 2017). Sea spray aerosols contain salts, organic material (fatty acids, monosaccharides, polysaccharides and siliceous material) and trace elements in both organic and inorganic forms, including N and P (Cochran *et al* 2017).

It has been demonstrated that some elements like P (Graham *et al* 1979), but also marine bacteria and

viruses (Aller *et al* 2005), can be enriched in sea spray aerosols during natural bubbling of the surface seawater (outgazing) induced by the overlying wind. Sea spray and ocean bacteria and viruses can penetrate inland and affect coastal ecosystems (Aller *et al* 2005, von Glasow 2008, von Glasow *et al* 2013). Gong *et al* (2002) estimated residence times in the marine boundary layer for supercoarse, coarse and fine sea spray aerosols of about 30 min, of the order of few hours, and of days to weeks, respectively, which allows small sea spray particles to be transported for large distances in the atmospheric circulation.

### 2.2.3. Bioaerosols

Bioaerosols include airborne particles of biogenic origin (e.g. bacteria, viruses, fungi, fungal spores) or various fragments or products released from living organisms (e.g. pollen) (Ariya *et al* 2009). Their sizes range from 10 nm to roughly 100 $\mu$m depending on their origin. Until recently attention has been given to bioaerosols because of their impact on human health (causing or enhancing diseases and allergies), on the spread of organisms, some of which might be pathogenic for humans, allowing genetic exchange between habitats and geographic shifts of biomes, and on climate (acting as ice-nucleating agents). These impacts are summarized in the comprehensive review by Fröhlich-Nowoisky *et al* (2016) and will not be further discussed here, where we focus on cloud chemistry which has received less attention to date. Observations indicate that there are significant emissions of bioaerosols from the sea surface (Aller *et al* 2005, Wilson *et al* 2015) as well as from terrestrial ecosystems (Despres *et al* 2012, Fröhlich-Nowoisky *et al* 2016).

Total global fluxes of bioaerosols are estimated as between 35 Tg yr$^{-1}$ (Fröhlich-Nowoisky *et al* 2016) and 1000 Tg yr$^{-1}$ (Jaenicke 2005). Spanning almost two orders of magnitude, this uncertainty requires reduction. Bioaerosols carry several trace elements that are present in biological material, such as N and P, in bioavailable forms, making a significant contribution to their atmospheric biogeochemical cycles (Kanakidou *et al* 2012, 2016, Myriokefalitakis *et al* 2016 and references therein). Specifically, they contribute about 9 Tg N yr$^{-1}$ (range 0.6–18.6 Tg N yr$^{-1}$), or about 8% of the total N emissions (Kanakidou *et al* 2012), and about 0.156 Tg P yr$^{-1}$, or about 50% of the primary bioavailable P emissions and about 10% of the total P emissions (Myriokefalitakis *et al* 2016). However, large uncertainties are associated with these estimates of the amounts bioaerosols emitted (Burrows *et al* 2009, Myriokefalitakis *et al* 2017) as well as their P and N content relative to C. The P and N content of bioaerosols has been used to derive their emissions, solubility and atmospheric ageing that converts insoluble to soluble material (Kanakidou *et al* 2012). More precisely, their N:C and P:C elemental ratios have been observed to range by over one and two orders of magnitude, respectively (Kanakidou *et al* 2012 and references therein). In addition, bacteria are considered as rather insoluble aerosols, in contrast to pollen grains and fungal spores that contain many highly polar sugars and sugar alcohols (Ariya *et al* 2009). It is worth mentioning the observed coexistence of bioaerosols and dust aerosols during dust events, as indicated by measurements of airborne microorganisms in the eastern Mediterranean and the west coast of the Atlantic Ocean at levels two to three times higher under dust conditions than during clear atmospheric conditions (Griffin *et al* 2001, 2007). These measurements are supported by the observations of highly water-soluble organic nitrogen amino acids in the dust outflows of the Sahara and Gobi deserts (Mace *et al* 2003, Wang *et al* 2013).

### 2.2.4. Volcanoes

Volcanoes are important contributors to both volcanic ash and sulfur dioxide emissions, with passive degassing contributing about 20% on top of total anthropogenic $SO_2$ emissions to the present day (Klimont *et al* 2013, Boucher 2015, Carn *et al* 2017). Although the volcanic contribution to the S budget is more important than to the other co-emitted materials (water, halogens, $CO_2$), the joint contribution of all emitted species can have a different impact in the atmosphere than the changes induced by $SO_2$ due to changes in atmospheric chemistry (LeGrande *et al* 2016). Rauch and Pacyna (2009) estimated that volcanic emissions are a greater contributor to the emissions of some metals (Fe, Ni, Cr and Al) than natural biomass combustion sources of these metals. On the basis of volcanic plume observations, Mahowald *et al* (2008) estimated the volcanic global source of P to be about 0.006 Tg P yr$^{-1}$. Although, on a global scale, volcanic ash is a small source of P, regional impacts on ocean nutrient distributions and marine productivity have been detected that are the result of concurrent injections of volcanic S, N, Fe and P (Uematsu *et al* 2004, Henson *et al* 2013, Olgun *et al* 2013). An upper limit to the P and Fe emissions from volcanic eruptions of 0.218 Tg P yr$^{-1}$ and 0.305 Tg Fe yr$^{-1}$, respectively, can be derived by using the volcanic ash content in Fe, P and $NH_x$ measured by Duggen *et al* (2007) and the $NH_x$ estimate of emissions from volcanic eruptions. The $NH_x$ flux can be derived from Uematsu *et al* (2004) concurrent observations of $NH_x$ and $SO_2$ during volcanic eruptions and the estimate of global $SO_2$ emissions from volcanoes (Boucher 2015).

In addition to volcanic eruptions (Benitez-Nelson *et al* 2003), meteors (Johnson 2001) can also deliver Fe to the atmosphere in the form of iron oxides, which are also potentially available to marine biota, but these emissions make a negligible contribution to the global Fe budget and are not considered in global models.

### 2.2.5. Biomass burning and fossil fuel combustion sources

In terms of mass, dust and sea-salt aerosols are by far (two orders of magnitude) the largest aerosol emissions

on the global scale when considering the $PM_{10}$ aerosol fraction (Boucher 2015). However, combustion processes emit more soluble, and thus more bioavailable, aerosols (Ito 2013, 2015a). Recently the contribution of coarse aerosols to biomass burning emissions has been pointed out (Luo *et al* 2008, Wang *et al* 2014).

Open fires can be both natural and anthropogenic in origin (Bowman *et al* 2009, Keywood *et al* 2011). They emit large amounts of aerosols, mainly black and organic carbon. Combustion processes also emit organic and inorganic trace gases that can form secondary aerosols (organic, sulfate and nitrate), as well as trace elements like Fe and P that are contained in the burnt biomass. According to Rauch and Pacyna (2009), the largest anthropogenic emissions of Al, Fe and Pb to the atmosphere are from fossil fuel combustion, while those of Ag, Cr, Cu, Ni and Zn are from industrial metal production. Gerst and Graedel (2008) estimated that, assuming a similar per capita use of metals as currently, in the future the amount of global in-use metal stocks required could be as high as three to nine times those existing at present. Therefore, anthropogenic inputs of these metals to the environment are expected to increase in the future.

While there is consensus that primary P sources from combustion processes make a significant contribution to global P fluxes in the atmosphere, in particular when the soluble fraction of P is concerned (Mahowald *et al* 2008), the estimates of the global strength of the combustion source vary by about an order of magnitude, between 0.1 and 2.5 Tg P $yr^{-1}$ (Mahowald *et al* 2008, Tipping *et al* 2014, Wang *et al* 2014, Brahney *et al* 2015, Myriokefalitakis *et al* 2016 and references therein). The reason for the divergence in the estimates is the consideration of different forms of P (i.e. residual or P-containing ash, gaseous or particulate P produced during combustion processes) and different size distributions of the emitted P-containing particulate matter, in particular consideration of significant combustion emissions (Wang *et al* 2014) or natural emissions (Tipping *et al* 2014, Brahney *et al* 2015) in the supercoarse (>10 $\mu$m) mode.

Biomass burning (Guieu *et al* 2005) and anthropogenic combustion processes, such as oil and coal fly ash (Luo *et al* 2008, Sedwick *et al* 2007), emit aerosols that contribute to atmospheric concentrations of Fe close to source regions but also over the open ocean (Sholkovitz *et al* 2012). Fe contained in oil fly ash has been observed to be associated with ferric sulfate salts and is thus very soluble (77%–81%) (Schroth *et al* 2009). Lower solubility has been measured for coal fly ash (20%–25%; Chen *et al* 2012) and even lower solubilities for biomass burning (~18%) (Bowie *et al* 2009). Total Fe emissions from combustion sources (biomass burning, fossil fuel, domestic and agricultural waste burning) have been estimated by Luo *et al* (2008) based on observed correlations between Fe and black carbon concentrations at 1.07 Tg Fe $yr^{-1}$ from biomass burning and 0.66 Tg Fe $yr^{-1}$ from industrial combustion. Ito (2013) has estimated the emissions of Fe from shipping to be 100 times lower, equal to about 0.016 Tg Fe $yr^{-1}$ for the year 2001. Wang *et al* (2015b) have evaluated total Fe emissions from fossil fuel and biomass combustion as being almost five times higher, at 5.3 Tg $yr^{-1}$ (90% confidence of 2.3–12.1 Tg $yr^{-1}$; averaged for the period 1960–2007). The largest estimates account for 72% emissions from combustion in the supercoarse mode, sizes at which aerosols, as already discussed, are expected to have only local impact since they are removed quickly by gravitational settling.

#### 2.2.6. *Agriculture*

Agricultural activities that use fertilizers and insecticides are known to emit aerosols and precursor gases. In particular, ammonia, nitrogen oxides and nitrous oxide are emitted from fertilized soils and livestock into the atmosphere, and ammonia and nitrogen oxides can produce aerosols (Pozzer *et al* 2017, Lelieveld *et al* 2015, Bauer *et al* 2016), which in turn, after atmospheric transport and via transformation, can return to the surface by deposition and fertilize ecosystems (Duce *et al* 2008). In addition the use of insecticides (e.g. organophosphates; FAO 2001 www.fao.org/faostat/) is a source of organic P particles entering the atmosphere (Kanakidou *et al* 2012).

Based on the above discussion, the primary emissions of N, P and Fe per source category are summarized in table 1.

### 2.3. Secondary sources—multiphase chemistry

Chemical transformation of sulfur dioxide, nitrogen oxides, ammonia and volatile organic compounds in the atmosphere leads to the formation of aerosols. This can occur by the formation of gas phase oxidation products like sulfuric acid, nitric acid and multifunctional organic compounds. Such compounds can nucleate ($H_2SO_4/H_2O$, $H_2SO_4/H_2O/NH_3$ and extremely low-volatility highly oxidized organics) to produce new particles (Zhang *et al* 2012, Kulmala *et al* 2013, Riccobono *et al* 2014, Dunne *et al* 2016, Kirkby *et al* 2016) in the atmosphere or partition onto existing ones (Seinfeld and Pandis 2006). They thus change the mass, size, composition and physicochemical and optical properties of the aerosol. Chemical ageing of aerosols through multiphase reactions also leads to particle growth, by modifying aerosols in the aqueous phase of the atmosphere (e.g. Pöschl and Shiraiwa 2015).

Di-nitrogen ($N_2$) is abundant in the atmosphere and is converted to reactive nitrogen by bacteria ($NH_4^+$, $NO_3^-$), lightning (NO) or anthropogenic activities (mainly as NO, $NO_2$, $HNO_3$, $NH_3$, $N_2O$); this is then assimilated by living organisms. Reactive nitrogen is also an important driver of atmospheric chemistry, since the availability of $NO_x$ ($NO + NO_2$) controls tropospheric ozone chemistry. In the atmosphere $NO_x$ is chemically converted to organic nitrogen compounds and $HNO_3$; together with (primarily)

**Table 1.** Summary of source estimates for total N ($NO_x/NO_3^-$, $NH_3/NH_4^+$, organic N), P(inorganic and organic P) and Fe (in Tg N $yr^{-1}$, Tg P $yr^{-1}$ and Tg Fe $yr^{-1}$, respectively). A range is provided, where available, with a suggested estimate in parenthesis. For details see in the text and the table footnotes.

| Sources | Nitrogen[a] | Phosphorus | Iron |
|---|---|---|---|
| Desert dust | 0.1–4.2 (0.3) | 0.23[c]–3.8[b] (1.1) | 35–115 (35)[b] |
| Soil and lightning | 6–23[d] (14) | | |
| Ocean (gases and sea spray) | 8.9–34.7 (14.4) | 0.005–2.71 (0.01)[g] | |
| Bioaerosols | 0.6–18.6 (9.0) | 0.002–2.13 (0.156) | 0.001–0.05 (0.001) |
| Volcanoes | 0.4–1.3 (0.9)[h] | 0.006–0.218 (0.01)[h] | 0.008–0.305[i] |
| Biomass burning | 15.6–44.06 (19.4) | 0.071–2.5[e,f] (0.1) | 1.07–5.3[e] (1.2) |
| Terrestrial anthropogenic | 60.3–77.3 (62.5) | | 0.66–0.77 |
| Shipping | 5.3 | | 0.015–0.016 |
| Total | 105.2–198.2 (126) | 0.5–9.5 (1.38) | 36.8–121.4[e] (42.1[b]) |

[a] Including organic nitrogen and gases.
[b] Neglecting super coarse particles.
[c] Lower limit from Wang *et al* (2014).
[d] Vinken *et al* (2014) and Nault *et al* (2017).
[e] Including supercoarse particles for biomass burning emissions.
[f] Lower limit from Mahowald *et al* (2008); upper limit from Wang *et al* (2014).
[g] Without phosphine emissions: lower limit from Mahowald *et al* (2008); upper limit from Kanakidou *et al* (2012) supplementary material.
[h] As $NH_x$, estimated based on Uematsu *et al* (2004) and Boucher (2015).
[i] Lower limit based on Mahowald *et al* (2008); upper limit estimated using Duggen *et al* (2007) volcanic ash content and $NH_x$ estimate of emissions from volcanic eruptions from this table.

sulfuric acid this contributes to atmospheric acidity, which controls the partitioning of $HNO_3/NO_3^-$ to the particulate phase. Ammonia has important emissions to the atmosphere, similar to or even higher than $NO_x$, depending on the region and year, and is the main neutralizing gas for these acidic compounds (Seinfeld and Pandis 2006). The availability of ammonia, together with environmental factors like temperature and relative humidity, controls the amount of ammonium and nitrate aerosols.

Multiphase chemistry is also well known to make a significant contribution to atmospheric sulfate production by oxidation of the dissolved sulfur dioxide to $SO_4^{2-}$ via reactions mainly with $H_2O_2$ and $O_3$. Transition metals play an important role in this conversion when photochemical processes are slow (at mid to high latitudes during winter) (Seinfeld and Pandis 2006, Alexander *et al* 2009, Harris *et al* 2013). Indeed, several metals have been measured in the atmospheric aqueous phase (aerosol water, fog, cloud and rain), among which Fe and Cu are the most important chemically when taking into account the measured concentrations and reactivity. There, the presence of the transition metal ions of Fe, Cu and Mn affects $HO_x$ (OH, $HO_2$, $H_2O_2$) concentrations and recycling, and their involvement in 'Fenton' reactions with $H_2O_2$ is an important source of radicals in the aqueous phase (Sedlak *et al* 1997).

A large variety of organic volatile compounds (VOCs) of anthropogenic and biogenic origin have the potential to form secondary organic aerosol (SOA) (Kanakidou *et al* 2005, Hallquist *et al* 2009). Biogenic VOCs, including aldehydes, ketones, alcohols and terpenoides, are emitted to the atmosphere mainly by vegetation; the largest single compound emitted is isoprene (Guenther *et al* 2012). Gas phase oxidation of organic compounds with several carbon atoms in their molecules and subsequent partitioning of their products to the aerosol phase has been found to contribute to the formation of SOA (Kanakidou *et al* 2005, Hallquist *et al* 2009, Shrivastava *et al* 2017), while multiphase organic photochemistry is also able to produce SOA (Blando and Turpin 2000) from the oxidation of smaller molecules such as acetylene (Volkamer *et al* 2009, Lim *et al* 2010). Chamber and field observations show that acidity of aerosols increases SOA formation and that sulfate esters are formed during the oxidation of isoprene in the presence of $SO_4^{2-}$. The formation of SOA from isoprene and monoterpenes is also observed to be mediated by anthropogenic $SO_2$ and $NO_x$ emissions through the presence of $SO_4^{2-}$ in aerosols and $NO_3$ radical chemistry (Xu *et al* 2015b). Therefore, $SO_4^{2-}$ is involved in the transfer of biogenic volatile organic compounds as gas-phase reaction products to the condensed phase and has been suggested to be important in the formation of humic-like substances (HULIS) in ambient aerosols (Graber and Rudich 2006, Surratt *et al* 2007).

Multiphase chemical reactions produce oxygenated organics and thus increase the O:C content of aerosols, reconciling model results with observations. For this reason, the O:C ratio has been suggested as a marker for aqueous multiphase chemistry (Waxman *et al* 2013). Glyoxal could make a significant contribution to the mass of ambient organic aerosol (OA) after hydration through multiphase chemistry that favors oxidation to form organic ligands like oxalic acid (Lim *et al* 2010, Ervens and Volkamer 2010, Myriokefalitakis *et al* 2011) and oligomerization reactions even in the absence of acidity (Wang *et al* 2010, Zhang *et al* 2012). Di-acids are important components of water-soluble organic C. They thus affect the water associated with aerosols and the aerosol pH. They also act as bidentate (chelating) ligands forming complexes with metals like

Fe and Cu, capturing the potential toxic free ions into less harmful forms for ecosystems, facilitating metal solubilization and providing a metal buffering capacity that maintains the activities of free metal ions at a natural level against relatively small perturbations of metals in the marine environment (Hirose and Sugimura 1985, Hirose 2006).

Atmospheric reactions of inorganic nitrogen (nitrogen oxides and ammonia) with organic compounds in the gas and the aqueous/aerosol phases can lead to the formation of organic nitrogen compounds and subsequent transfer of inorganic nitrogen to the aerosol phase (Atkinson and Arey 2003, Ervens and Volkamer 2010). Recent laboratory investigations have shown that photosensitizers can initiate aerosol growth in the presence of gaseous volatile organic compounds, in particular the imidazole derivatives, like imidazole-2 carboxaldehyde, that are formed by reaction of glyoxal with ammonium cations (Rossignol *et al* 2014). Dark reactions including acid-catalyzed aerosol chemistry of hydronium or ammonium ions, which protonate epoxide and carbonyl groups thus enabling attack by nucleophiles such as water, $SO_4^{2-}$, $NH_3$ and $NO_3^-$, may be responsible for the ring opening mechanism of epoxides, organosulfate formation by epoxides and carbonyls and C–N-containing light-absorbing organic species as part of the 'brown carbon' pool (Surratt *et al* 2010, McNeill 2015, Laskin *et al* 2015). Night-time chemistry driven by $NO_3$ radicals also produces organic nitrogen in the aerosol phase that was found to be 5%–12% of OAs during the summer months (Xu *et al* 2015a). Kiendler-Scharr *et al* (2016) found that 34%–44% of nitrate in submicron aerosols in Europe is organic nitrogen and a significant fraction of it can be attributed to gas-phase $NO_3$ radical night-time chemistry. The secondarily formed organic N contributes to the atmospheric deposition of organic N, which in turn makes up around 20%–25% of the global total of soluble N deposition (Cornell 2011, Kanakidou *et al* 2012, Jickells *et al* 2013).

Overall, the SOA source estimates span more than an order of magnitude from 12 to about 500 Tg yr$^{-1}$; these estimates were made using different assumptions of SOA volatility and SOA fragmentation that also affects volatility (Tsigaridis *et al* 2014, Shrivastava *et al* 2017). SOA formation in both cloud and aerosol water has been estimated to range between 13 and 47 Tg yr$^{-1}$, and between a small loss (−0.4 Tg yr$^{-1}$) and a significant source (13 Tg yr$^{-1}$), respectively (Myriokefalitakis *et al* 2011, Lin *et al* 2014). A significant amount of organic N is attached to these aerosols. According to global model estimates, this amount lies between about 3 and 18 Tg N yr$^{-1}$ and contains both oxidized and reduced organic N (Kanakidou *et al* 2016, Ito *et al* 2014). The secondary production of organic N can be of similar magnitude to primary emissions of organic N from specific sources, as has been estimated for biomass burning (Ito *et al* 2015).

## 3. Aerosol processing: solubilization of nutrients and the role of acidity

Desert dust contains a large variety of minerals and metals, most of them in insoluble form (Claquin *et al* 1999, Nickovic *et al* 2012). However, to be bioavailable to ecosystems elements have to be in soluble form (or in nanoparticles of diameter smaller than 0.2 $\mu$m). In addition, atmospheric aerosol observations show the presence of noticeable amounts of soluble elements such as Fe (Sholkovitz *et al* 2012) and P (Mackey and Paytan 2009, Baker *et al* 2006a). The mechanisms that convert insoluble material to the soluble material that is readily bioavailable to ecosystems remain under investigation.

Uptake of Fe, the fourth most abundant element in the Earth's crust, by living organisms is indeed limited because it is mainly present in the form of insoluble iron oxides. However, various cellular mechanisms have evolved to capture Fe from the environment in biologically useful forms. For instance, microbes excrete siderophores to capture Fe as six-coordinate complexes with Fe(III), or they use other mechanisms to reduce iron from the insoluble ferric form ($Fe^{3+}$) to the soluble ferrous form ($Fe^{2+}$) (Abbaspour *et al* 2014). Conversion of insoluble to soluble forms of nutrients (i.e. solubilization), requires acidic conditions, and for metals it can be followed by chelation (reversible complexation of a ligand to a metal ion), which further increases solubilization. Such conditions may be produced by soil microorganisms (Arrieta and Grez 1971, Alori *et al* 2017, Mackey and Paytan 2009) or by abiotic chemical reactions in the atmosphere (Ooki and Uematsu 2005, Shi *et al* 2011a, 2012, Nenes *et al* 2011, Stockdale *et al* 2016). Both biotic and abiotic processes proceed initially by the production of inorganic or organic acids, with a simultaneous decrease of pH, and of the ligands needed to react with minerals and release nutrients to the solution.

Indeed, solubilization of the Fe and P present in atmospheric aerosols is found to be affected by atmospheric acidity (Shi *et al* 2011a, 2012) and to increase with the acidity of the aerosol and cloud water (Theodosi *et al* 2010). Furthermore, analysis of observations using aerosol equilibrium simulations has supported the importance of the aerosol acidity for the conversion of Fe(III) to the more soluble Fe(II) and the role of anthropogenic sulfate in modulating acidity in the Pacific (Meskhidze *et al* 2003). Fe requires much more acidic conditions than P in order to be solubilized (van Cappellen and Berner 1991, Guidry and Mackenzie 2003, Nenes *et al* 2011, Myriokefalitakis *et al* 2015, 2016, Stockdale *et al* 2016).

Three different chemical mechanisms for Fe solubilization have been identified so far: proton-driven, ligand-driven (Paris *et al* 2011, Paris and Desboeufs 2013) and photo-induced reductive Fe solubilization (Chen and Grassian 2013). Reductive dissolution

involves conversion of Fe(III) to Fe(II) by electron transfer (Larsen and Postma 2001, Fu *et al* 2010) and is significantly accelerated in the presence of Fe(II) or Fe(II) ligand complexes (Litter *et al* 1994). Al-Abadleh (2015) reviewed the bulk and surface chemistry of Fe in the presence of HULIS and reported direct photoreductive formation of Fe(II) or organic Fe complexes in photoreductive experiments, with the highest rates being observed at low pH values. Shi *et al* (2012) made a comprehensive laboratory investigation of the factors that affect Fe solubilization from dust aerosols. Their results point to acid processing rather than cloud processing as a prime mechanism that increases the solubility of dust Fe during transport in the atmosphere. Furthermore, laboratory studies have shown that Fe solubilization from minerals occurs on different timescales—from hours to weeks depending on the particle size and mineralogical composition (Shi *et al* 2011b). For instance, in acidic conditions octahedral cations were found to be released more readily than tetrahedral cations and the preference for metal release depends on the metal–O bond; in particular the number of protons needed to release the metal depends on the metal valence (Bibi *et al* 2011). Thus phyllosilicates are solubilized much faster than aluminosilicates (Ito and Shi 2016a). Laboratory experiments have also shown that the formation of mononuclear bidentate complexes of oxalic acid with Fe surfaces enhances dissolution of Fe in dust and combustion aerosols more than sulfuric acid when both acids are present in the atmosphere (Chen and Grassian 2013). The breaking of Fe–O bonds at the mineral surface controls the rate of dissolution of Fe, which increases as pH decreases. Chen and Grassian (2013) also found that when oxalate concentrations are low the dissolution of Fe is suppressed because dissolved Fe competes with surface Fe for complexation.

Experiments on laboratory dust solubilization have shown that solubilization of P and $Ca^{2+}$, i.e. release from dust, depends on the amount of $H^+$ in the dust aerosol water, i.e. the aqueous layer surrounding the dust particle (Stockdale *et al* 2016). At low $H^+$ concentrations the release of P is controlled by water volume alone, while above $10^{-4}$ mol. $g^{-1}$ an approximately linear relationship exists between P solubilization and $H^+$ concentration until the acid reactive phosphate pool of the dust aerosol is exhausted. $Ca^{2+}$ behaves similarly, but with lower threshold values for $H^+$ than P. Indeed, $H^+$ can react with $PO_4^{3-}$ and the OH or F groups of apatite minerals at the crystal surface, thus weakening the $Ca^{2+}$ bonds and mobilizing $PO_4^{3-}$ from the crystal surface (Christoffersen and Christoffersen 1981). Such a mechanism of desert dust solubilization under polluted conditions has been suggested to explain the observed $PO_4^{3-}$ levels over the eastern Mediterranean, a typical region where Saharan dust can interact with polluted air masses from Europe and the Middle East (Nenes *et al* 2011).

Natural aerosols, especially the larger sized ones, are enriched in cations like $Ca^{2+}$, $Mg^{2+}$ and $Al^{3+}$ (dust), $Na^+$, $K^+$ and $Mg^{2+}$ (sea spray), and $K^+$ (biomass burning). These aerosols show more basic characteristics than anthropogenic aerosols, which are smaller in size, richer in acids and thus have a more acidic behavior than natural aerosols (Bougiatioti *et al* 2016). This reduced acidity of coarse aerosols significantly suppresses dissolution of Fe and P, while it favors the partitioning of nitrate to the aerosol phase (Weber *et al* 2016, Karydis *et al* 2016). It also partially explains the observed inverse relationship between Fe solubility and particle size (Baker and Jickells 2006, Ito and Feng 2010).

Dust aerosols coated by acidic compounds (e.g. sulfates and nitrates), which form by heterogeneous uptake of $SO_2$ and $HNO_3$ during atmospheric transport (Bauer *et al* 2007), show increased Fe solubility compared with fresh dust particles, in particular in fine mode (Meskhidze *et al* 2005). Such particles can be transported and deposited in remote regions, for example over the Atlantic and Pacific oceans (Baker *et al* 2006c, Sedwick *et al* 2007). In line with these findings, a positive correlation between Fe solubility and sulfur emissions has been observed for acidic atmospheric samples collected at urban sites (Oakes *et al* 2012), supporting substantial atmospheric processing or anthropogenic combustion sources of soluble Fe.

Atmospheric acidity also affects nutrient deposition via its control on the partitioning of $HNO_3/NO_3^-$ to the aerosol phase (Weber *et al* 2016). Indeed, in order to be captured into the aerosol phase, $NO_3^-$ requires an aerosol pH higher than 2 to start transfer to the aerosol phase; at a pH of about 4 or higher it is mostly present in the aerosol phase, due to the semi-volatile character of $NH_4NO_3$. Such pH constraints can be fulfilled by coarse dust aerosols, where non-volatile cations like $Ca^{2+}$ keep pH levels relatively high, or on biomass burning aerosols, where $K^+$ cations play a similar role. On the other hand, anthropogenic or acid-coated fine aerosols suppress $HNO_3/NO_3^-$ partitioning to the aerosol phase. Because of the different removal rates of $HNO_3$ and $NO_3^-$ through deposition, and thus removal lifetimes, aerosol acidity, via its impact on $HNO_3/NO_3^-$ partitioning, will also affect the distribution of $HNO_3/NO_3^-$ deposition.

## 4. Nutrient biogeochemical cycles (including organic fractions)

Atmospheric aerosols, either directly emitted or chemically formed in the atmosphere, undergo atmospheric transport and physical and chemical transformations before being deposited to the surface where they release nutrients. Atmospheric aerosols are therefore a significant component of nutrient biogeochemical cycles, and the spatiotemporal variability of the

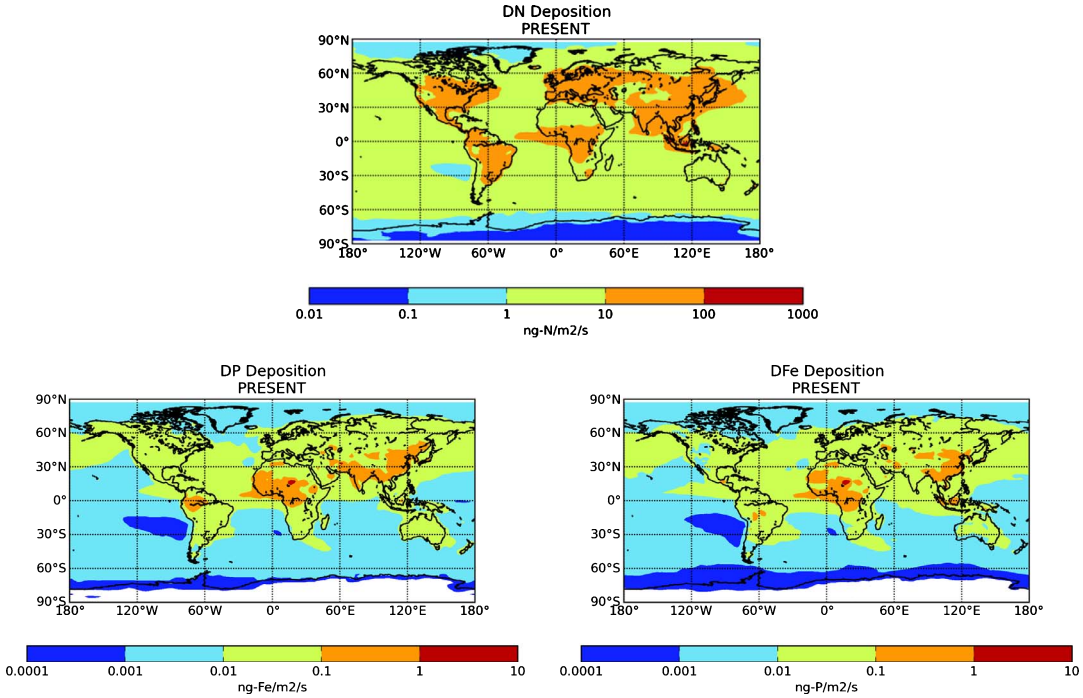


**Figure 2.** Deposition fluxes of soluble N (DN), soluble P (DP) and soluble Fe (DFe) for the present day (year 2005 for DN and year 2008 for DP and DFe).

atmospheric deposition fluxes and their intensity depend on atmospheric transport and ageing. In the following we will focus on the N, P and Fe cycles, as these elements are essential nutrients for ecosystems and are known to limit primary productivity depending on their availability and location.

N, P and Fe are integral parts of living organisms. N is an essential component of amino acids, which are the structural basis of proteins, and is also contained in several other biological molecules such as nucleotides and nucleic acids (deoxyribonucleic acid or DNA and ribonucleic acid or RNA), making it necessary for life (Galloway *et al* 2008). In addition, N-containing molecules carry electrons and hydrogen, both of which are necessary for organismal functions such as respiration and photosynthesis. Indeed, N is a component of chlorophyll, where N atoms bind $Mg^{2+}$ at the center of the chlorophyll structure. P is also essential for the formation of DNA and RNA; it is required for bone formation and for adenosine triphosphate (ATP), which stores energy in cells and supplies it to cellular processes, and for hemoglobin, which transports oxygen in blood (Smil 2000). The availability of P strongly influences the fixation of inorganic C into cellular biomass by photosynthetic organisms. P supply is a major factor governing the productivity of ecosystems, especially during long-term ecosystem development (Benitez-Nelson 2000). Fe is an essential element for almost all living organisms as it participates in a wide variety of metabolic processes, including oxygen transport, DNA synthesis and electron transport (Abbaspour *et al* 2014). The importance of Fe comes from its involvement in redox (reduction/oxidation) reactions and its ability to reversibly change its oxidation state by electron transfer, which varies depending on the ligand with which Fe is complexed (Guerinot 1994). Several enzymes involved in photosynthesis, respiration and N fixation (Twining *et al* 2004) require Fe, which makes it an important micronutrient for marine organisms; shortage of Fe can limit primary productivity over large regions of the ocean, the so-called high-nutrient/low-chlorophyll (HNLC) regions (Martin *et al* 1991, Jickells *et al* 2005, Boyd *et al* 2005, Moore *et al* 2013).

### 4.1. Nitrogen

Motivated by the importance of the biogeochemical cycle of N for life on our planet, several global modeling efforts have been made to simulate the global atmospheric N cycle (Galloway *et al* 2004, Neff *et al* 2002, Lamarque *et al* 2013, Vet *et al* 2014, Dentener *et al* 2006a, 2006b, 2014, Kanakidou *et al* 2012, 2016, Ito *et al* 2014, 2015).

Recently, Kanakidou *et al* (2012) provided a methodology that enabled construction of the global atmospheric cycle of organic N (and organic P) based on observations of the N:C (and P:C) content of aerosols and on the organic aerosol global atmospheric cycle as computed by their global model. They estimated that organic N is about 50% anthropogenic and amounts to about 20%–40% of total soluble N deposition (figure 2), with large regional variability (figure 3) (Kanakidou *et al* 2012, 2016), in agreement with observations (Cornell 2011, Jickells *et al* 2013). These simulations take into account the $HNO_3/NO_3^-$ pH-driven partitioning to the aerosol phase as well as the

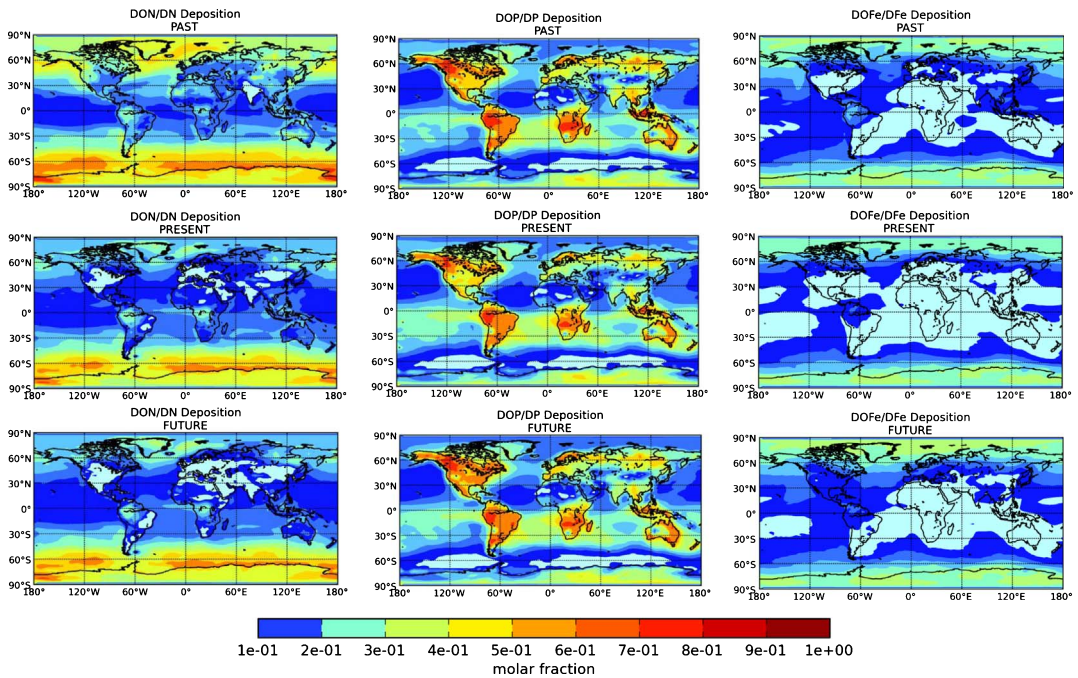


**Figure 3.** Fractions of soluble organic N (DON) to total soluble N (DN) deposition (left panels); of soluble organic P (DOP) to total soluble P (DP) deposition (middle panels); of Fe–oxalate complexes to total soluble Fe deposition, note that only cloud water chemistry is considered as a source of Fe–oxalate (DOFe) for these simulations (right panels) with emissions: top, past (emission year 1850); middle, present (year 2005 for N and year 2008 for P and Fe); bottom, future (emission year 2050 for N, emission year 2100 for P and Fe).

formation of N-containing SOA that occurs when sufficient $NO_x$ is available. Based on the latter process, about 10% of the emitted $NO_x$ are deposited as organic N instead of inorganic N, as was suggested in most earlier global modeling studies (Dentener *et al* 2006a, Lamarque *et al* 2013). They also evaluated that about 40% of the total N deposition is in the form of atmospheric aerosols.

Since the start of industrialization, human activities have dramatically increased the amounts of N emitted to the atmosphere and deposited to the surface, modifying the N biogeochemical cycle (Galloway *et al* 2008). Using the anthropogenic and biomass-burning Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP) historical emissions and the Representative Concentration Pathway (RCP6.0 and RCP8.5) future emissions scenarios in a global model, and accounting for the organic N as explained above, human-driven N deposition has been shown to have globally increased by about 80 Tg N $yr^{-1}$ since 1850. This change, from about 50 Tg N $yr^{-1}$ in 1850 to about 130 Tg N $yr^{-1}$ in 2005, is more pronounced over the land (almost a three-fold increase), where most of the anthropogenic sources are found, compared with over the ocean (a two-fold increase) (Kanakidou *et al* 2016). A similar global increase (by a factor of 1.9) has been estimated by Brahney *et al* (2015). Projections for the year 2050 show a further increase in N deposition by less than 5 Tg N $yr^{-1}$ (to about 135 Tg N $yr^{-1}$) due to the implementation of air pollution abatement strategies leading to a reduction in $NO_x$ and $SO_2$ emissions (Kanakidou *et al* 2016). These deposition estimates also include the emission and re-deposition of marine organic N and ammonium, which will not lead to a net increase in marine productivity (Jickells *et al* 2017). The contribution of soluble organic N to total soluble N has been reduced from 40% in the past to 20% currently, and is projected to remain at roughly this level in the future (figure 3). Large uncertainties are associated with these results because they are based on an incomplete understanding of the N content of organics and neglect future changes in biogenic emissions driven by climate. The future projections also indicate significant changes in the regional distribution of N deposition and its chemical composition, with reduced compounds gaining in importance relative to oxidized ones (figure 4), but small changes in the global total N flux (Lamarque *et al* 2013, Kanakidou *et al* 2016). A qualitative change in the chemical composition of the deposited N is also found in particular with regard to $NO_3^-$ deposition, which has increased since 1850 and is projected to be reduced in the future due to reductions in $SO_2$ and $NO_x$ emissions to improve air quality. This is not the case for $NH_x$, which is projected to continue to increase due to lack of a legislative requirement to reduce its emissions. Total organic N deposition is projected to remain almost unchanged in the future.

This difference in the composition of N deposition is expected to affect ecosystem growth, since ammonium is taken up more quickly by vegetation than nitrate, while little is known about how or how

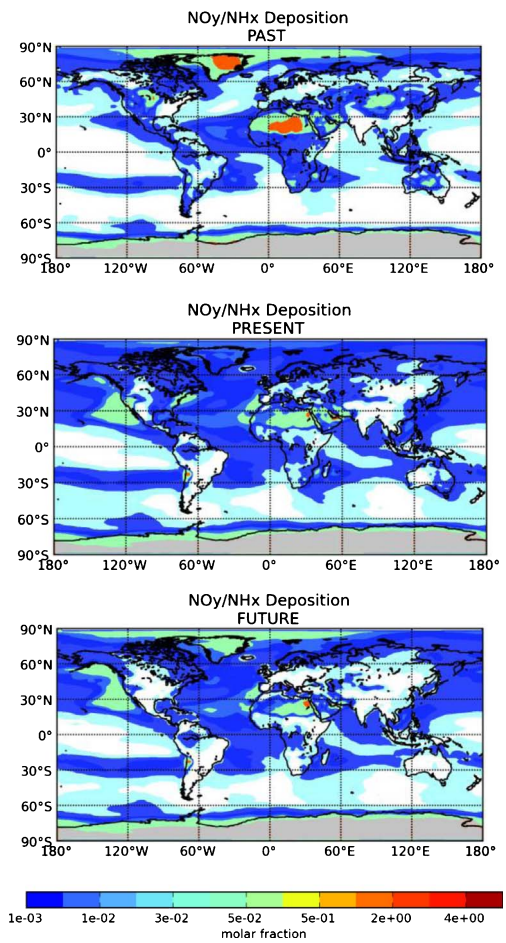


**Figure 4.** Change in the composition of soluble inorganic N deposition due to anthropogenic emissions and biomass burning represented by the molar ratio of $NO_y/NH_x$. $NO_y$ contains $NO_x$, HONO, $HNO_4$, $N_2O_5$, $HNO_3$, particulate $NO_3^-$; $NH_x$ contains $NH_3$ and particulate $NH_4^+$ (PAST = emission year 1850; PRESENT = emission year 2005; FUTURE = emission year 2050).

fast organic N is assimilated by organisms. The form of N that is used by an organism should reflect that organism's enzymatic systems for absorbing and incorporating N (Rice 1992). Plants that take up $NO_3^-$ will need to reduce it to $NH_4^+$ before it can be used for synthesis of amino acids and other nitrogenous organic compounds: this transformation, however, requires energy. Nitrate reductase is involved in the first step of the reduction of $NO_3^-$ into a form that can be used by plants, and is the enzyme that controls the ability of plants to use $NO_3^-$; therefore those species that use mostly $NO_3^-$ as their N source should have relatively high levels of nitrate reductase activity (NRA) (Rice 1992). For algae, Sigee (2005) reported that because uptake of ammonia does not require energy, and there is no induction period for enzymes required for assimilation when both nitrate and ammonia are available, ammonia is the preferred choice. The energy required for nitrate reduction is derived from photosynthesis. Organic compounds can be only used via specialized enzymatic processes (Gattuso and Hansson 2012). In the ocean, organic N is converted to dissolved organic N by heterotrophic bacteria, and is then remineralized to $NH_4^+$ by several potential processes such as enzymatic breakdown and degradation of biomass (Sigee 2005). Therefore, the model-simulated changes in the composition of the deposited N (Kanakidou *et al* 2016) might favor the development of species that are more able to assimilate the available forms of deposited N that have increased.

Large continental areas of the world are subject to N deposition fluxes that exceed 10 kg N $ha^{-1}$ $yr^{-1}$, i.e. that are more than an order of magnitude greater than natural fluxes and exceed the critical loads that have detrimental impacts on ecosystems (Bobbink and Hettelingh 2011, Galloway *et al* 2008). N availability limits primary productivity over large areas of the global ocean (Wang *et al* 2015a, Duce *et al* 2008). Thus, in low-N marine ecosystems atmospheric deposition of N enhances primary productivity (e.g. Zamora *et al* 2010). Duce *et al* (2008) estimated that the human-induced increase in deposition of atmospheric N to the oceans may account globally for up to 3% of the annual new oceanic primary productivity, in parallel with export into suboxic or anoxic zones that will increase marine emissions of $N_2O$ to the atmosphere (Suntharalingam *et al* 2012). Higher contributions of atmospheric N deposition to marine productivity have been estimated for semi-enclosed marine ecosystems such as the Mediterranean Sea, for which atmospheric deposition of N (and P) may account for up to 35%–60% of new production (Christodoulaki *et al* 2016). Recently, Jickells *et al* (2017) used these updated estimates of N influx external to the ocean to re-evaluate the global impact of anthropogenic atmospheric deposition of N on C sequestration by marine ecosystems. Their new estimate of annual marine primary productivity is much lower than earlier estimates, and this effect is almost compensated by $N_2O$ emissions. Interestingly, potential ecological shifts through changes in nutrient regimes have been also reported, driven by atmospheric deposition of nutrients (e.g. Krishnamurthy *et al* 2009, Chien *et al* 2017, Wang *et al* 2015a). These results show the complexity of the effects of atmospheric deposition that involve several feedback mechanisms and need to be evaluated synergistically.

### 4.2. Phosphorus

Unlike atmospheric reactive N, P (and Fe) is present in the atmosphere mainly in the aerosol phase, with the exception of a few phosphines which are rather scarce in the environment. P has a variety of natural sources including dust, volcanoes, sea spray, freshwater wetlands (that emit phosphine) (Glindemann *et al* 2005, Han *et al* 2011) and biomass burning. It is also produced by a number of human activities, including deforestation, P mining and agricultural practices (fertilizers and insecticides). The human-driven emissions increase the solubility of atmospheric P and cause the

accumulation of P in soils and aquatic environments (Mackey and Paytan 2009). The first estimates of the total global deposition fluxes of P based on extrapolations from scarce observations varied between 3 and 4 Tg P $yr^{-1}$ (Graham and Duce 1979, Smil 2000). Of this amount, only a fraction is soluble or in the nanoparticle size range that is readily available to ecosystems.

The first global simulations of the atmospheric P cycle were focused on dust sources, considering a fixed 10% solubility of P on dust aerosols, 100% solubility of P in volcanic emissions and 50% from other sources (Mahowald *et al* 2008). Recent studies have included dust, combustion and biological aerosols in the super-coarse mode as P sources (Tipping *et al* 2014, Wang *et al* 2014, Brahney *et al* 2015), thus accounting for the total P in the atmosphere. Brahney *et al* (2015) argue that aquatic organisms have evolved numerous ways to rapidly acquire P from organic molecules, therefore in the long-term all P would potentially be available.

Recently, Myriokefalitakis *et al* (2016) provided the first global modeling study of the P atmospheric cycle with an explicit parameterization of P solubilization on mineral dust under acidic conditions in the atmosphere, occurring both in the aerosol and in cloud water. They showed that neglecting the dissolution of P degrades the comparison of model results with observations. They also found that the chemical processing of dust contributes about one-third (0.14 Tg P $yr^{-1}$) of the global atmospheric source of soluble P; this has increased over the past 150 years by about 70% due to changes in anthropogenic and biomass burning emissions that have affected atmospheric acidity. Future reductions of about 30% were projected for 2100 due to the implementation of air quality regulations that also affect atmospheric acidity. The present-day global annual soluble P deposition flux of 0.45 Tg P $yr^{-1}$ was calculated to have a strong spatial and temporal variability, with about 40% of this amount being deposited over the oceans (figure 2). This soluble P deposition flux, which accounts for soluble organic P and phosphate, is almost double the estimate of phosphate emissions by Mahowald *et al* (2008), in which neither organic P nor the chemical processing of dust aerosol were considered. Accounting for changes in both the anthropogenic emissions of P and the solubilization of P due to chemical processing, Myriokefalitakis *et al* (2016) estimated that about 20% of the increase in the soluble P flux was due to changes in anthropogenic emissions since 1850, and projected a reduction of ~15% by 2100 due to changes in anthropogenic emissions. They also evaluated that the contribution of bioaerosols to the total deposition of bioavailable P to the marine environment can seasonally exceed 50% regionally, indicating the existence of potentially important interactions between terrestrial and marine ecosystems.

The computed contribution of soluble organic P to the bioavailable dissolved deposition (DP) varies between 37% and 40%, with the lowest contribution occurring at present. As discussed in section 2, the contribution of biological particles to bioavailable P is also considerable, as pointed out by Myriokefalitakis *et al* (2016).

The computed atmospheric deposition of readily bioavailable P over the global ocean varies between 0.096 Tg P $yr^{-1}$ (Mahowald *et al* 2008) and 0.17 Tg P $yr^{-1}$. While riverine inputs mainly affect coastal regions, atmospheric deposition is a source of nutrients for the open sea (e.g. Okin *et al* 2011).

While N and Fe are limiting nutrients for large fractions of the ocean (Moore *et al* 2013), P is known to co-limit primary productivity over certain regions like the Mediterranean (Krom *et al* 1991), where the P limitation has been attributed to the anomalously high N:P ratio in the atmospheric deposition fluxes (Markaki *et al* 2010). The disproportionate increase of atmospheric deposition of anthropogenic N over P in the eastern Mediterranean can explain such behavior (Christodoulaki *et al* 2016) and the atmospheric fluxes of N and P may have induced a total increase in phytoplankton biomass of 16% over the past 150 years. Furthermore, Richon *et al* (2017) simulations for the entire Mediterranean Sea have shown that atmospheric deposition of N and dust P increases primary productivity over vast regions on average by 30%–50% and that the fertilization effects are transmitted along the biological chain. They also calculated that the dust input of P increases primary productivity by up to 30% when surface stratification occurs, results that are in agreement with those of Christodoulaki *et al* (2013) for the eastern Mediterranean.

Similarly to the Mediterranean case, the increased anthropogenic N flux to the north Pacific Ocean and the observed resulting increase in surface nitrate levels provide an excess N input compared with P and this is expected to potentially induce a P limitation in that area (Kim *et al* 2014). Brahney *et al* (2015), analyzing data from 700 upland lakes globally, found a P limitation induced by the much faster atmospheric flux of anthropogenic N. They also suggested that despite the smaller changes in the flux of P compared with that of N, P may have a greater impact on primary productivity, because, on average, based on the Redfield ratio, one unit of increased P deposition has 16 times the influence of one unit of N deposition (Brahney *et al* 2015). Human-induced P limitation has also been recorded in the forests of south China, where both N and P deposition have increased but the increase in anthropogenic N deposition is faster than that of P deposition.

### 4.3. Iron

Fe is present in the aerosol and water phases of the atmosphere. Mineral dust is the dominant source of Fe, contributing ~95% of the Fe atmospheric load on a global scale while the remaining ~5% is contributed by volcanoes, biomass burning and anthropogenic

combustion processes (Mahowald *et al* 2009). However, Fe from non-dust sources is more soluble than mineral dust on aerosols (Luo *et al* 2008, Ito 2013, Ito 2015a).

Global emissions estimates of total Fe vary by a factor of three, from 37–115 Tg Fe $yr^{-1}$ (Mahowald *et al* 2009, Ito and Kok 2017, Ito and Shi 2016b, Ito and Xu 2014, Johnson and Meskhidze 2013, Luo *et al* 2008, Myriokefalitakis *et al* 2015, Wang *et al* 2015b), with a small fraction (1–2 Tg-Fe $yr^{-1}$) emitted as soluble Fe (Mahowald *et al* 2017). Representation of Fe in global models has continuously improved over the years by accounting for the variable mineralogy of dust emissions and different Fe contents in the various minerals (Nickovic *et al* 2012, Journet *et al* 2014). Combustion emissions have also been considered in more detail (Luo *et al* 2008, Ito 2013, 2015, Wang *et al* 2015b), but this has increased the uncertainty range for these emissions estimates, which vary between ~2 and 5.3 Tg Fe $yr^{-1}$. The uncertainty in the Fe emission estimates has been evaluated to be a factor of four to five for both dust and combustion sources (Luo *et al* 2008).

Solubilization through atmospheric processing has recently been parameterized in models with ever-increasing detail: Luo *et al* (2008) performed a sensitivity study; Johnson and Meskhidze (2013) considered only dust solubilization and scaled oxalate to $SO_4^{2-}$; Myriokefalitakis *et al* (2015) explicitly calculated oxalate through the multiphase chemistry of carbonyls (Myriokefalitakis *et al* 2011), proton-promoted Fe solubilization for three different types of Fe minerals and combustion aerosols in both aerosol water and cloud droplets and ligand-promoted Fe solubilization in cloud droplets only; Ito (2015b) accounted for proton-promoted solubilization considering one type of Fe mineral, and oxalate dissolution processes accounted for the photo-reductive dissolution process but for both dust and combustion aerosols. This latter mechanism has been found to have only a minor impact on Fe solubilization. Myriokefalitakis *et al* (2015) calculated a solubilization flux of 0.175 Tg Fe $yr^{-1}$ that is half of the total primary soluble Fe emissions from both mineral and combustion sources in their model. About 22% of this solubilization flux is attributed to organic ligands.

Overall, modeled estimates of total Fe deposition fluxes to the ocean range between 7 and 11 Tg Fe $yr^{-1}$ (Ito and Kok 2017, Ito and Shi 2016b, Ito and Xu 2014, Johnson and Meskhidze 2013, Luo *et al* 2008, Myriokefalitakis *et al* 2015, Wang *et al* 2015b) and show significant spatial and temporal variability. Soluble Fe deposition fluxes to the ocean have been reported to range between 0.11 and 0.34 Tg Fe $yr^{-1}$ (Johnson and Meskhidze 2013, Myriokefalitakis *et al* 2015, Ito 2015a, Ito and Shi 2016a). The uncertainty in the simulated deposition fluxes of soluble Fe to the ocean has been evaluated to range between −50% and +150%; this is associated with the uncertainty in Fe-containing minerals commonly found on dust (Johnson and Meskhidze 2013).

Humans have significantly modified the Fe atmospheric cycle (Tagliabue *et al* 2017) and atmospheric deposition by increasing direct emissions of Fe from industrial (e.g. smelting) and combustion processes (Mahowald *et al* 2009), such as combustion of fossil fuels and coal, and the acidity of atmospheric aerosols, which affects the conversion of mineral Fe to more soluble and thus bioavailable forms. Myriokefalitakis *et al* (2015), based on historical and projected emission scenarios (as for P), calculated that atmospheric deposition fluxes of soluble Fe have more than doubled since 1850 due to increases in the primary non-dust emissions and in dust-Fe solubilization. They also projected that the deposition flux of soluble Fe will decrease by about 25% due to reductions in primary anthropogenic and biomass burning emissions as well as in the dust-Fe solubilization flux. Similarly, Ito and Xu (2014) estimated that the improvement in air quality projected for the future will lead to a decrease of the deposition of filterable Fe (soluble and particulate of diameter $<0.02\,\mu$m) from Fe-containing mineral dust to the eastern North Pacific due to lower acidification in Asian dust, which is mainly associated with the reduction of $NO_x$ emissions. Ito and Shi (2016a), accounting for dust and combustion emission of Fe, estimated that the soluble Fe flux to the ocean has increased from 0.05–0.07 Tg Fe $yr^{-1}$ in the pre-industrial period to 0.11–0.12 Tg Fe $yr^{-1}$ at present due to air pollution. These numbers do not account for the oxalate-promoted solubilization of Fe on dust aerosols. Myriokefalitakis *et al* (2015) have estimated that Fe–oxalate complexes, produced by ligand-promoted dust-Fe solubilization in cloud water, made a global contribution of between 7% and 18% to soluble Fe deposition, with the smallest contribution calculated for the present and the highest when considering anthropogenic emissions in 1850 (figure 3). This fraction has to be considered as a lower limit estimate since ligand-promoted Fe solubilization in aerosol water was not considered in their study.

Note, however, that these studies do not take into account changes in dust emissions for past and projected estimations. Dust emissions have been estimated to have increased by about 40% over the last century (Mahowald *et al* 2017). Overall, the changes due to atmospheric pollution as well as the projected air quality improvements are expected to affect the oceanic productivity, in particular over the high-nutrient/low-chlorophyll oceanic regions.

The external supply of Fe in the open ocean can affect a number of biogeochemical processes, as nicely reviewed by Tagliabue *et al* (2017). Fe deposition can significantly stimulate N fixation and biological C export on a global scale. Increased Fe deposition has also been proposed to lead to increased regional respiration and productivity and expansion of minimum oxygen zones (Ito *et al* 2016), thus affecting

life in the ocean. Fe supply also has an impact on ecosystem biodiversity. For instance, a high Fe supply favors algae with red-line plastids (diatoms and cryptomonads) to have a lower Fe:P content than algae with green-line plastids, such as chlorophytes and prasinophytes (Twining and Baines 2013). Furthermore, phytoplankton in the Fe-rich tropical Atlantic exhibit Fe:P stoichiometries more than five times higher than in the Southern Ocean under low-Fe conditions (Twining and Baines 2013). In the Fe-poor Southern Ocean, ferric reductases enable the use of the more dominant organically complexed Fe pool by phytoplankton, and this strategy appears to be common in organisms adapted to a 'bioavailability envelope' (Tagliabue *et al* 2017).

## 5. Importance of humans in changing atmospheric acidity and nutrient biogeochemical cycles

As discussed earlier, anthropogenic emissions of atmospheric acid precursors ($NO_x$ and $SO_2$) have been increasing over the past 150 years and only started to decline in the last 30 years due to measures taken to mitigate air pollution (Lamarque *et al* 2010, van Vuuren *et al* 2011). In parallel, emissions of ammonia, the main alkaline gas that neutralizes these acids in the atmosphere, have also changed, although at different rates than $NO_x$ emissions (Lamarque *et al* 2010). This is because of the absence of direct regulations on $NH_3$ emissions which have been indirectly affected, at least in Europe, by changes in agricultural practices since 1990 (EEA 2010). These emission changes have also modified the acidity of the various atmospheric compartments (gases, aerosols, clouds, rain), which responded differently to these changes because different solution densities and different fractions of pollutant emissions are involved (Driscoll *et al* 2016, Pascaud *et al* 2016, Watmough *et al* 2016, Weber *et al* 2016). This led to changes in all three nutrients discussed here, namely N, P, and Fe. Because of the different mechanisms for the dependence of atmospheric deposition of the soluble fraction of N, P and Fe on atmospheric acidity, it is expected that the relative abundances of the soluble fraction of these nutrients in the deposition flux has also been modified since 1850 and will change in the future. Indeed, based on recent results obtained with the same global model for N (Kanakidou *et al* 2016), P (Myriokefalitakis *et al* 2016) and Fe (Myriokefalitakis *et al* 2015) (total soluble fluxes shown in figure 2 for present-day simulations), the changes in the N:P:Fe stoichiometry of the deposition fluxes can be derived. These changes reflect not only chemistry-driven modifications of the deposition fluxes but also those due to the primary anthropogenic emissions of these nutrients.

N deposition, in particular nitrate deposition, is also affected by aerosol acidity since the partitioning of $HNO_3/NO_3^-$ to the aerosol phase is prohibited under very acidic conditions (Weber *et al* 2016). Because of the high deposition rates of $HNO_3$ when compared with fine aerosols (Brook *et al* 1997), Kajino *et al* (2008) concluded that atmospheric deposition of total $NO_3^-$ (sum of $HNO_3$ gas and $NO_3^-$ particulates) can increase, modulated by the presence of $SO_4^{2-}$, even when $NO_x$ emissions remain constant or slightly decrease. This behavior is confirmed by the analysis of global simulations of the atmospheric N cycle (Kanakidou *et al* 2016) which show that at present a larger fraction of total $NO_3^-$ is in the gas phase (as $HNO_3$) than has been in the 'past' and will be in the 'future'. As a consequence, the lifetime of the total $NO_3^-$ due to atmospheric deposition is calculated to have decreased by 35% from the 'past' to the present day and to increase by about 20% in the 'future'. These changes in partitioning between gas and aerosol phases are modulated by changes in acidity, with key roles played by $SO_2$ and $NH_3$ emissions, and lead to changes in the geographical pattern of emissions.

Global model simulations enable a distinction between the two factors (chemical processing and primary emissions) affecting the soluble fractions of Fe and of P in atmospheric deposition. In particular, the proton- and ligand-driven solubilization of dust-Fe (Myriokefalitakis *et al* 2015) and the acidity-driven solubilization of dust-P (Myriokefalitakis *et al* 2016) have been considered. The deposited soluble fluxes of Fe (and P) carried by dust alone, calculated as the sum of the initially emitted soluble dust-nutrients and the solubilized amounts during chemical processing (ageing) in the atmosphere, were found to be higher at present by 12% and 24% for Fe and P, respectively, compared with 'past' depositions (anthropogenic and biomass burning emissions of the year 1850) (Lamarque *et al* 2010). An almost equivalent decrease was estimated for when these emissions reach 2100 levels ('future'), as in the RCP6.0 scenario (van Vuuren *et al* 2011). These decreases are driven by much larger changes in the solubilized amounts during atmospheric ageing and are entirely due to the modification of atmospheric acidity and the ligand content of aerosol and cloud water induced by the changes in anthropogenic and biomass burning emissions.

As already mentioned, Fe and P show a different dependence on atmospheric acidity—Fe requires a more acidic environment to solubilize than P—so the molar ratio of the atmospheric deposition of soluble Fe to that of soluble P associated with dust aerosols is expected to be affected by the changes in anthropogenic and biomass burning emissions. The results of Myriokefalitakis *et al* (2016) indicate significant increases from the 'past' to the present in the ratio of soluble Fe to soluble inorganic phosphate (DFe/DIP) when accounting for both primary and secondary sources (figure 5), in particular over tropical oceans in the outflow of desert dust emissions mixed with the atmosphere from Asian and Central American

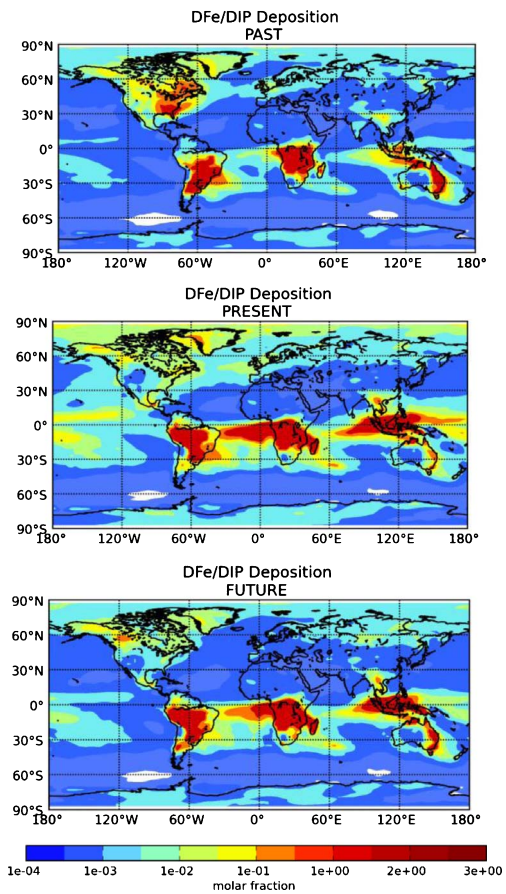


**Figure 5.** Ratios of deposition fluxes of DFe/DIP (soluble Fe to soluble inorganic P from all sources) (past = emission year 1850, present = emission year 2008, future = emission year 2100).

pollution and tropical biomass burning. In the 'future' precursor emissions should continue to be limited by legislation so the solubilization of dust-Fe will be almost back to 'past' levels, with only small differences that are mainly due to biomass burning emissions. On the other hand, over North America, where air quality has improved since the 'past' due to the limitation of extensive coal combustion and will continue to improve due to the applied legislation, decreases in DFe/DIP are calculated from the 'past' to present and to the 'future'. However, these results have to be interpreted with caution and used only as a qualitative demonstration of the impact of acidity on the deposition of nutrients carried by dust, since they are associated with significant uncertainties in the aerosol acidity calculations, in particular due to the mixing state description of aerosols. In addition, as discussed earlier, changes in nutrients can favor certain species over others and so the overall functioning of ecosystems, while others can adapt to the new conditions (Guerinot 1994). The evaluation of such impacts requires the use of coupled land/atmosphere or land/air–sea exchange modeling and the consideration of nutrient ratios that deviate from Redfield stoichiometry.

## 6. Summary and recommendations

This review, based on a compilation of current experimental and modeling studies, has documented the importance of atmospheric processing via multiphase chemistry for the formation of nutrients or their transformation to forms that are readily bioavailable to ecosystems. This process needs to be further understood and considered when modeling atmospheric deposition of nutrients.

It has also shown that there is a clear consensus on the importance of the organic fraction of nutrients as an integral part of the atmospheric cycles of the main nutrients considered here (N, P, Fe), and that atmospheric aerosols are the key carriers of these components. Interestingly, bioaerosols have been found to make a significant contribution to atmospheric sources of N and P (Kanakidou *et al* 2012, Myriokefalitakis *et al* 2016), indicating potentially significant interactions between terrestrial and marine ecosystems. However, further experimental and modeling studies are needed to provide accurate quantification of organic nutrient sources and impacts on ecosystems. In particular, measurements in remote locations are logistically difficult but invaluable for the documentation and understanding of atmospheric processing of aerosols. There is also the need for better characterization of organic nutrients present in atmospheric aerosols and their association with organic matter present in the ocean and the ecosystem response to the corresponding atmospheric inputs.

Little is also known about the bioavailability of the organic material that penetrates to ecosystems via atmospheric deposition; it is expected that when there is a shortage of inorganic nutrients organisms will search for other forms of nutrients (organics) even if they might be less easy to assimilate. It is also expected that those which are able to adapt to the environmental changes will be favored over others in such a case. It has been suggested that changes in the relative composition of atmospherically deposited nutrients are driving human-induced limitations of the ecosystems to specific nutrients. These modifications are also favoring the development of certain species over others and impacting on the overall functioning of ecosystems (Guerinot 1994).

Furthermore, we have focused here on the abiotic solubilization of nutrients. However, it is worth mentioning the dual role of microbes in the atmosphere, which contribute to bioaerosols as carriers of nutrients (mainly N and P) but also as mediators increasing or reducing the bioavailability of nutrients in the environment (Mackey and Paytan 2009). The presence of microbes in soils has been used to explain the occurrence of bioavailable Fe and P, and soil microbes could therefore also have a potential for use in sustainable agricultural development (Alori *et al* 2017). However, to our knowledge, no work has been done

on the presence of such microbes in atmospheric aerosols and their potential contribution to further solubilization of nutrients present in aerosols during atmospheric transport. Instead, the focus has been on the solubilization of trace elements under acidic conditions driven by abiotic chemical reactions forming acids and ligands in atmospheric aerosols.

Finally, it has been seen that although Redfield stoichiometry is commonly used as a first step in identifying the limiting nutrient for ecosystem development, the functioning of several species deviates from Redfield stoichiometry, in particular those that are able to adapt to nutrient stress conditions. Therefore there is a close link between community structure and the average relative proportions of nutrients in suspended and sinking particles in the ocean that requires a deeper understanding (Twining *et al* 2004). These impacts, including the contribution of organic nutrients to atmospheric deposition, need to be understood and taken into account in Earth system modeling with a new 'non-Redfield' approach to modeling biogeochemistry.

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## References

Abbaspour N, Hurrell R and Kelishadi R 2014 Review on iron and its importance for human health *J. Res. Med. Sci.* **19** 164–74
Aiken A C *et al* 2008 O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry *Environ. Sci. Technol.* **42** 4478–85
Al-Abadleh H A 2015 Review of the bulk and surface chemistry of iron in atmospherically relevant systems containing humic-like substances *RSC Adv.* **5** 45785–811
Alexander B, Park R J, Jacob D J and Gong S 2009 Transition metal-catalyzed oxidation of atmospheric sulfur: global implications for the sulfur budget *J. Geophys. Res. Atmos.* **114** D02309
Aller J Y, Kuznetsova M R, Jahns C J and Kemp P F 2005 The sea surface microlayer as a source of viral and bacterial enrichment in marine aerosols *J. Aerosol Sci.* **36** 801–12
Alori E T, Glick B R and Babalola O O 2017 Microbial phosphorus solubilization and its potential for use in sustainable agriculture *Front. Microbiol.* **8** 1–8
Altieri K E, Hastings M G, Peters A J and Sigman D M 2012 Molecular characterization of water soluble organic nitrogen in marine rainwater by ultra-high resolution electrospray ionization mass spectrometry *Atmos. Chem. Phys.* **12** 3557–71
Anderson L D, Faul K L and Paytan A 2010 Phosphorus associations in aerosols: what can they tell us about P bioavailability? *Mar. Chem.* **120** 44–56
Ariya P A, Sun J, Eltouny N A, Hudson E D, Hayes C T and Kos G 2009 Physical and chemical characterization of bioaerosols—implications for nucleation processes *Int. Rev. Phys. Chem.* **28** 1–32
Arneth A *et al* 2010 Terrestrial biogeochemical feedbacks in the climate system *Nat. Geosci.* **3** 525–32
Arrieta L and Grez R 1971 Solubilization of iron-containing minerals by soil microorganisms *Appl. Microbiol.* **22** 487–90
Atkinson R and Arey J 2003 Atmospheric degradation of volatile organic compounds *Chem. Rev.* **103** 4605–38
Attwood A R *et al* 2014 Trends in sulfate and organic aerosol mass in the southeast US: impact on aerosol optical depth and radiative forcing *Geophys. Res. Lett.* **41** 7701–9
Aumont O and Bopp L 2006 Globalizing results from ocean *in situ* iron fertilization studies *Glob. Biogeochem. Cycles* **20** GB2017
Aumont O, Bopp L and Schulz M 2008 What does temporal variability in aeolian dust deposition contribute to sea-surface iron and chlorophyll distributions? *Geophys. Res. Lett.* **35** L07607
Baker A R and Jickells T D 2006 Mineral particle size as a control on aerosol iron solubility *Geophys. Res. Lett.* **33** L17608
Baker A R, French M and Linge K L 2006a Trends in aerosol nutrient solubility along a west–east transect of the Saharan dust plume *Geophys. Res. Lett.* **33** L07805
Baker A R, Jickells T D, Witt M and Linge K L 2006b Trends in the solubility of iron, aluminium, manganese and phosphorus in aerosol collected over the Atlantic Ocean *Mar. Chem.* **98** 43–58
Baker A R, Jickells T D, Witt M and Linge K L 2006c Trends in the solubility of iron, aluminium, manganese and phosphorus in aerosol collected over the Atlantic Ocean *Mar. Chem.* **98** 43–58
Baker A R, Adams C, Bell T G, Jickells T D and Ganzeveld L 2013 Estimation of atmospheric nutrient inputs to the Atlantic Ocean from 50°N to 50°S based on large-scale field sampling: iron and other dust-associated elements *Glob. Biogeochem. Cycles* **27** 755–67
Bauer S E, Mishchenko M I, Lacis A A, Zhang S, Perlwitz J and Metzger S M 2007 Do sulfate and nitrate coatings on mineral dust have important effects on radiative properties and climate modeling? *J. Geophys. Res. Atmos.* **112** D06307
Bauer S E, Tsigaridis K and Miller R 2016 Significant atmospheric aerosol pollution caused by world food cultivation *Geophys. Res. Lett.* **43** 5394–400
Benitez-Nelson C R 2000 The biogeochemical cycling of phosphorus in marine systems *Earth-Science Rev.* **51** 109–35
Benitez-Nelson C R, Vink S M, Carrillo J H and Huebert B J 2003 Volcanically influenced Fe and Al cloud water deposition to Hawaii *Atmos. Environ.* **37** 535–44

Bibi I, Singh B and Silvester E 2011 Dissolution of illite in saline-acidic solutions at 25 °C *Geochim. Cosmochim. Acta* **75** 3237–49

Blando J D and Turpin B J 2000 Secondary organic aerosol formation in cloud and fog droplets: a literature evaluation of plausibility *Atmos. Environ.* **34** 1623–32

Bobbink R and Hettelingh J P 2011 *Review and revision of empirical critical loads and dose-response relationships* Coordination Centre for Effects, National Institute for Public Health and the Environment (www.rivm.nl/cce)

Boucher O 2015 *Atmospheric Aerosols Properties and Climate Impacts* (New York: Springer)

Bougiatioti A, Nikolaou P, Stavroulas I, Kouvarakis G, Weber R, Nenes A, Kanakidou M and Mihalopoulos N 2016 Particle water and pH in the eastern Mediterranean: source variability and implications for nutrient availability *Atmos. Chem. Phys.* **16** 4579–91

Boulanger K J 2015 Decadal trends in atmospheric organic aerosol: analysis of network data and method development *Thesis* (Harvard, MA: Massachusetts Institute of Technology, Department of Civil and Environmental Engineering)

Bowie A R, Lannuzel D, Remenyi T A, Wagener T, Lam P J, Boyd P W, Guieu C, Townsend A T and Trull T W 2009 Biogeochemical iron budgets of the Southern Ocean south of Australia: decoupling of iron and nutrient cycles in the subantarctic zone by the summertime supply *Glob. Biogeochem. Cycles* **23** GB003500

Bowman D M J S *et al* 2009 Fire in the Earth system *Science* **324** 481–4

Boyd P W *et al* 2005 FeCycle: attempting an iron biogeochemical budget from a mesoscale $SF_6$ tracer experiment in unperturbed low iron waters *Glob. Biogeochem. Cycles* **19** GB002494

Brahney J, Mahowald N M, Ward D S, Ballantyne A P and Neff J C 2015 Is atmospheric phosphorus pollution altering global alpine Lake stoichiometry? *Glob. Biogeochem. Cycles* **29** 1369–83

Brook J R, Di-Giovanni F, Cakmak S and Meyers T P 1997 Estimation of dry deposition velocity using inferential models and site-specific meteorology—uncertainty due to siting of meteorological towers *Atmos. Environ.* **31** 3911–9

Burrows S M, Butler T, Joeckel P, Tost H, Kerkweg A, Poeschl U and Lawrence M G 2009 Bacteria in the global atmosphere—Part 2: modeling of emissions and transport between different ecosystems *Atmos. Chem. Phys.* **9** 9281–97

van Cappellen P and Berner R A 1991 Fluorapatite crystal growth from modified seawater solutions *Geochim. Cosmochim. Acta* **55** 1219–34

Carlton A G and Turpin B J 2013 Particle partitioning potential of organic compounds is highest in the Eastern US and driven by anthropogenic water *Atmos. Chem. Phys.* **13** 10203–14

Carlton A G, Turpin B J, Altieri K E, Seitzinger S, Reff A, Lim H J and Ervens B 2007 Atmospheric oxalic acid and SOA production from glyoxal: results of aqueous photooxidation experiments *Atmos. Environ.* **41** 7588–602

Carlton A G, Turpin B J, Altieri K E, Seitzinger S P, Mathur R, Roselle S J and Weber R J 2008 CMAQ model performance enhanced when in-cloud secondary organic aerosol is included: comparisons of organic carbon predictions with measurements *Environ. Sci. Technol.* **42** 8798–802

Carn S A, Fioletov V E, Mclinden C A, Li C and Krotkov N A 2017 A decade of global volcanic $SO_2$ emissions measured from space *Sci. Rep.* **7** 44095

Carslaw K S, Boucher O, Spracklen D V, Mann G W, Rae J G L, Woodward S and Kulmala M 2010 A review of natural aerosol interactions and feedbacks within the Earth system *Atmos. Chem. Phys.* **10** 1701–37

Chen H and Grassian V H 2013 Iron dissolution of dust source materials during simulated acidic processing: the effect of sulfuric, acetic, and oxalic acids *Environ. Sci. Technol.* **47** 10312–21

Chen H, Laskin A, Baltrusaitis J, Gorski C A and Scherer M M 2012 Supporting information coal fly ash as a source of iron in atmospheric dust *Environ. Sci. Technol.* **46** 2113–20

Chien C T, Mackey K R M, Dutkiewicz S, Mahowald N M, Prospero J M and Pyatan A 2017 Effects of African dust deposition on phytoplankton in the western tropical Atlantic Ocean off Barbados *Glob. Biogeochem. Cycles* **30** 716–34

Christensen M W, Chen Y C and Stephens G L 2016 Aerosol indirect effect dictated by liquid clouds *J. Geophys. Res.* **121** 14636–50

Christodoulaki S, Petihakis G, Kanakidou M, Mihalopoulos N, Tsiaras K and Triantafyllou G 2013 Atmospheric deposition in the Eastern Mediterranean. A driving force for ecosystem dynamics *J. Mar. Syst.* **109–110** 78–93

Christodoulaki S, Petihakis G, Mihalopoulos N, Tsiaras K, Triantafyllou G and Kanakidou M 2016 Human-driven atmospheric deposition of N and P controls on the east Mediterranean marine ecosystem *J. Atmos. Sci.* **73** 1611–8

Christoffersen J and Christoffersen M R 1981 Kinetics of dissolution of calcium hydroxyapatite *J. Cryst. Growth* **53** 42–54

Chuang P Y, Duvall R M, Shafer M M and Schauer J J 2005 The origin of water soluble particulate iron in the Asian atmospheric outflow *Geophys. Res. Lett.* **32** GL021946

Claquin T, Schulz M and Balkanski Y J 1999 Modeling the mineralogy of atmospheric dust sources *J. Geophys. Res.* **104** 22243

Cochran R E *et al* 2017 Molecular diversity of sea spray aerosol particles: impact of ocean biology on particle composition and hygroscopicity *Chem.* **2** 655–67

Cornell S E 2011 Atmospheric nitrogen deposition: revisiting the question of the importance of the organic component *Environ. Pollut.* **159** 2214–22

Dentener F J *et al* 2006a Nitrogen and sulfur deposition on regional and global scales: a multimodel evaluation *Glob. Biogeochem. Cycles* **20** GB4003

Dentener F J *et al* 2006b The global atmospheric environment for the next generation *Environ. Sci. Technol.* **40** 3586–94

Dentener F J, Vet R, Dennis R L, Du E, Kulshrestha U C and Galy-Lacaux C 2014 Progress in monitoring and modelling estimates of nitrogen deposition at local, regional and global scales *Nitrogen Deposition, Critical Loads and Biodiversity: Proceedings of the International Nitrogen Initiative Workshop, Linking Experts of the Convention on Long-Range Transboundary Air Pollution and the Convention on Biological Diversity* ed M A Sutton, K E Mason, L J Sheppard, H Sverdrup, R Haeuber and W K Hicks (Dordrecht: Springer) pp 7–22

Despres V R *et al* 2012 Primary biological aerosol particles in the atmosphere: a review *Tellus B* **64** 15598

Driscoll C T, Driscoll K M, Fakhraei H and Civerolo K 2016 Long-term temporal trends and spatial patterns in the acid-base chemistry of lakes in the Adirondack region of New York in response to decreases in acidic deposition *Atmos. Environ.* **146** 5–14

Duce R A and Quinn J G 1972 Enrichment of heavy metals and organic compounds in the surface microlayer of Narragansett Bay, Rhode Island *Science* **176** 161–3

Duce R A *et al* 2008 Impacts of atmospheric anthropogenic nitrogen on the open ocean *Science* **320** 893–7

Duggent S, Croot P, Schacht U and Hoffmann L 2007 Subduction zone volcanic ash can fertilize the surface ocean and stimulate phytoplankton growth: evidence from biogeochemical experiments and satellite data *Geophys. Res. Lett.* **34** L01612

Dunne E M *et al* 2016 Global atmospheric particle formation from CERN CLOUD measurements *Science* **354** 1119–24

Ebling A M and Landing W M 2017 Trace elements in the sea surface microlayer: rapid responses to changes in aerosol deposition *Elem. Sci. Anth.* **5** 42

EEA 2010 *Ammonia ($NH_3$) Emissions* (Copenhagen: European Environmental Agency) (www.eea.europa.eu/data-and-maps/indicators/eea-32-ammonia-nh3-emissions-1)

Erel Y, Pehkonen S O and Hoffmann M R 1993 Redox chemistry of iron in fog and stratus clouds *J. Geophys. Res.* **98** 18423

Ervens B 2015 Modeling the processing of aerosol and trace gases in clouds and fogs *Chem. Rev.* **115** 4157–98

Ervens B and Volkamer R 2010 Glyoxal processing by aerosol multiphase chemistry: towards a kinetic modeling framework of secondary organic aerosol formation in aqueous particles *Atmos. Chem. Phys.* **10** 8219–44

Escribano J, Boucher O, Chevallier F, Huneeus N, Dynamique D M, Pierre U and Cnrs C 2017 Impact of the choice of the satellite aerosol optical depth product in a sub-regional dust emission inversion *Atmos. Chem. Phys.* **17** 7111–26

FAO 2001 www.fao.org/faostat/

Fröhlich-Nowoisky J *et al* 2016 Bioaerosols in the Earth system: climate, health, and ecosystem interactions *Atmos. Res.* **182** 346–76

Fu H, Cwiertny D M, Carmichael G R, Scherer M M and Grassian V H 2010 Photoreductive dissolution of Fe-containing mineral dust particles in acidic media *J. Geophys. Res.* **115** D11304

Fung I Y, Meyn S K, Tegen I, Doney S C, John J G and Bishop J K B 2000 Iron supply and demand in the upper ocean *Glob. Biogeochem. Cycles* **14** 281–95

Furutani H, Meguro A, Iguchi H and Uematsu M 2010 Geographical distribution and sources of phosphorus in atmospheric aerosol over the North Pacific Ocean *Geophys. Res. Lett.* **37** GL041367

Fuzzi S *et al* 2006 Critical assessment of the current state of scientific knowledge, terminology, and research needs concerning the role of organic aerosols in the atmosphere, climate, and global change *Atmos. Chem. Phys.* **6** 2017–38

Galloway J N *et al* 2004 Nitrogen cycles: past, present, and future *Biogeochem.* **70** 153–226

Galloway J N, Trends R, Townsend A R, Erisman J W, Bekunda M, Cai Z, Freney J R, Martinelli L A, Seitzinger S P and Sutton M A 2008 Transformation of the nitrogen cycle: potential solutions *Science* **320** 889–92

Gattuso J P and Hansson L 2012 Effects of acidification on pelagic organisms and ecosystems *Ocean Acidification* (Oxford: Oxford University Press) p 111

Gerst M D and Graedel T E 2008 In-use stocks of metals: status and implications *Environ. Sci. Technol.* **42** 7038–45

von Glasow R 2008 Pollution meets sea salt *Nat. Geosci.* **1** 291–2

von Glasow R *et al* 2013 Megacities and large urban agglomerations in the coastal zone: interactions between atmosphere, land, and marine ecosystems *Ambio.* **42** 13–28

Glindemann D, Edwards M, Liu J A and Kuschk P 2005 Phosphine in soils, sludges, biogases and atmospheric implications—a review *Ecol. Eng.* **24** 457–63

Goldstein A H and Galbally I E 2007 Known and unexplored organic constituents in the earth's atmosphere *Environ. Sci. Technol.* **41** 1514–21

Gong S L, Barrie L A and Lazare M 2002 Canadian aerosol module (CAM): a size-segregated simulation of atmospheric aerosol processes for climate and air quality models 2. Global sea-salt aerosol and its budgets *J. Geophys. Res. Atmos.* **107** D002004

Graber E R and Rudich Y 2006 Atmospheric HULIS: how humic-like are they? A comprehensive and critical review *Atmos. Chem. Phys.* **6** 729–53

Graham W F and Duce R A 1979 Atmospheric pathways of the phosphorus cycle *Geochim. Cosmochim. Acta* **43** 1195–208

Graham W F, Piotrowicz S R and Duce R A 1979 The sea as a source of atmospheric phosphorus *Mar. Chem.* **7** 325–42

Griffin D W, Garrison V H, Herman J R and Shinn E A 2001 African desert dust in the Caribbean atmosphere: microbiology and public health *Aerobiologia* **17** 203–13

Griffin D W, Kubilay N, Koçak M, Gray M A, Borden T C and Shinn E A 2007 Airborne desert dust and aeromicrobiology over the Turkish Mediterranean coastline *Atmos. Environ.* **41** 4050–62

Guenther A B, Jiang X, Heald C L, Sakulyanontvittaya T, Duhl T, Emmons L K and Wang X 2012 The model of emissions of gases and aerosols from nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions *Geosci. Model Dev.* **5** 1471–92

Guerinot M L 1994 Microbial iron transport *Annu. Rev. Microbiol.* **48** 743–72

Guidry M W and Mackenzie F T 2003 Experimental study of igneous and sedimentary apatite dissolution: control of pH, distance from equilibrium, and temperature on dissolution rates *Geochim. Cosmochim. Acta* **67** 2949–63

Guieu C, Bonnet S, Wagener T and Loe-Pilot M D 2005 Biomass burning as a source of dissolved iron to the open ocean? *Geophys. Res. Lett.* **32** GL022962

Guieu C *et al* 2014a The significance of the episodic nature of atmospheric deposition to low nutrient low chlorophyll regions *Glob. Biogeochem. Cycles* **28** GB004852

Guieu C, Ridame C, Pulido-Villena E, Bressac M, Desboeufs K and Dulac F 2014b Impact of dust deposition on carbon budget: a tentative assessment from a mesocosm approach *Biogeosciences* **11** 5621–35

Hallquist M *et al* 2009 The formation, properties and impact of secondary organic aerosol: current and emerging issues *Atmos. Chem. Phys.* **9** 5155–236

Han C, Geng J, Hong Y, Zhang R, Gu X, Wang X, Gao S and Glindemann D 2011 Free atmospheric phosphine concentrations and fluxes in different wetland ecosystems, China *Environ. Pollut.* **159** 630–5

Hand J L, Mahowald N M, Chen Y, Siefert R L, Luo C, Subramaniam A and Fung I 2004 Estimates of atmospheric-processed soluble iron from observations and a global mineral aerosol model: biogeochemical implications *J. Geophys. Res. D* **109** 1–21

Harris E *et al* 2013 Enhanced role of transition metal *Science* **340** 727–30

Heald C L, Kroll J H, Jimenez J L, Docherty K S, Decarlo P F, Aiken A C, Chen Q, Martin S T, Farmer D K and Artaxo P 2010 A simplified description of the evolution of organic aerosol composition in the atmosphere *Geophys. Res. Lett.* **37** GL042737

Heimburger A, Losno R and Triquet S 2013 Solubility of iron and other trace elements in rainwater collected on the Kerguelen Islands (South Indian Ocean) *Biogeosciences* **10** 6617–28

Henson S A, Painter S C, Penny Holliday N, Stinchcombe M C and Giering S L C 2013 Unusual subpolar North Atlantic phytoplankton bloom in 2010: volcanic fertilization or North Atlantic Oscillation? *J. Geophys. Res. Ocean.* **118** 4771–80

Herrmann H, Ervens B, Jacobi H W, Wolke R, Nowacki P and Zellner R 2000 CAPRAM2.3: A chemical aqueous phase radical mechanism for tropospheric chemistry *J. Atmos. Chem.* **36** 231–84

Hirose K 2006 Chemical speciation of trace metals in seawater: a review *Anal. Sci.* **22** 1055–63

Hirose K and Sugimura Y 1985 Role of metal-organic complexes in the marine environment *Mar. Chem.* **16** 239–47

Hoesly R M *et al* 2018 Historical 1750-2014 anthropogenic emissions of reactive gases and aerosols from the community emission data system (CEDS) *Geosci. Model Dev. Discuss.* **11** 369–408

Ito A 2013 Global modeling study of potentially bioavailable iron input from shipboard aerosol sources to the ocean *Glob. Biogeochem. Cycles* **27** GB004378

Ito A 2015a Atmospheric processing of combustion aerosols as a source of bioavailable iron *Environ. Sci. Technol. Lett.* **2** 70–5

Ito A 2015b Atmospheric processing of combustion aerosols as a source of bioavailable iron *Environ. Sci. Technol. Lett.* **2** 70–5

Ito A and Feng Y 2010 Role of dust alkalinity in acid mobilization of iron *Atmos. Chem. Phys.* **10** 9237–50

Ito A and Kok J F 2017 Do dust emissions from sparsely vegetated regions dominate atmospheric iron supply to the Southern Ocean? *J. Geophys. Res.* **122** 3987–4002

Ito A and Shi Z 2016a Delivery of anthropogenic bioavailable iron from mineral dust and combustion aerosols to the ocean *Atmos. Chem. Phys. Discuss.* **16** 85–99

Ito A and Shi Z 2016b Delivery of anthropogenic bioavailable iron from mineral dust and combustion aerosols to the ocean *Atmos. Chem. Phys.* **16** 85–99

Ito A and Xu L 2014 Response of acid mobilization of iron-containing mineral dust to improvement of air quality projected in the future *Atmos. Chem. Phys.* **14** 3441–59

Ito A, Lin G and Penner J E 2014 Reconciling modeled and observed atmospheric deposition of soluble organic nitrogen at coastal locations *Glob. Biogeochem. Cycles* **28** 617–30
Ito A, Lin G and Penner J E 2015 Global modeling study of soluble organic nitrogen from open biomass burning *Atmos. Environ.* **121** 103–12
Ito T, Nenes A, Johnson M S, Meskhidze N and Deutsch C 2016 Acceleration of oxygen decline in the tropical Pacific over the past decades by aerosol pollutants *Nat. Geosci.* **9** 443–7
Jaenicke R 2005 Abundance of cellular material and proteins in the atmosphere *Science* **308** 73
Jickells T D *et al* 2005 Global iron connections between desert dust, ocean biogeochemistry, and climate *Science* **308** 67–71
Jickells T D, Baker A R, Cape J N, Cornell S E and Nemitz E 2013 The cycling of organic nitrogen through the atmosphere *Phil. Trans. R. Soc. B* **368** 20130115
Jickells T D *et al* 2017 A reevaluation of the magnitude and impacts of anthropogenic atmospheric nitrogen inputs on the ocean *Glob. Biogeochem. Cycles* **31** 289–305
Jimenez J L *et al* 2009 Evolution of organic aerosols in the atmosphere *Science* **326** 1525–9
Johnson K S 2001 Iron supply and demand in the upper ocean: is extraterrestrial dust a significant source of bioavailable iron? *Glob. Biogeochem. Cycles* **15** 61–3
Johnson M S and Meskhidze N 2013 Atmospheric dissolved iron deposition to the global oceans: effects of oxalate-promoted Fe dissolution, photochemical redox cycling, and dust mineralogy *Geosci. Model Dev.* **6** 1137–55
Journet E, Desboeufs K V, Caquineau S and Colin J L 2008 Mineralogy as a critical factor of dust iron solubility *Geophys. Res. Lett.* **35** GL031589
Journet E, Balkanski Y and Harrison S P 2014 A new data set of soil mineralogy for dust-cycle modeling *Atmos. Chem. Phys.* **14** 3801–16
Kajino M, Ueda H and Nakayama S 2008 Secondary acidification: changes in gas-aerosol partitioning of semivolatile nitric acid and enhancement of its deposition due to increased emission and concentration of $SO_x$ *J. Geophys. Res. Atmos.* **113** D008635
Kanakidou M, Tsigaridis K, Dentener F J and Crutzen P J 2000 Human activity enhanced formation of organic aerosols by biogenic hydrocarbon oxidation *J. Geophys. Res.* **105** 9243–54
Kanakidou M *et al* 2005 Organic aerosol and global climate modelling: a review *Atmos. Chem. Phys.* **5** 1053–123
Kanakidou M *et al* 2012 Atmospheric fluxes of organic N and P to the global ocean *Glob. Biogeochem. Cycles* **26** GB3026
Kanakidou M, Myriokefalitakis S, Daskalakis N, Fanourgakis G, Nenes A, Baker A R, Tsigaridis K and Mihalopoulos N 2016 Past, present and future atmospheric nitrogen deposition *J. Atmos. Sci.* **73** 2039–47
Karydis V A, Tsimpidi A P, Pozzer A, Astitha M and Lelieveld J 2016 Effects of mineral dust on global atmospheric nitrate concentrations *Atmos. Chem. Phys.* **16** 1491–509
Keywood M *et al* 2011 In the air: biomass burning impacts in a changing climate *Crit. Rev. Environ. Sci. Technol.* **43** 40–83
Kiendler-Scharr A, Mesah A A, Friese E, Topping D, Prevot A S and Al E 2016 Ubiquity of organic nitrates from nighttime chemistry in the European submicron aerosol *Geophys. Res. Lett.* **43** 7735–44
Kim I, Lee K, Gruber N, Karl D M, Bullister J L, Yang S and Kim T 2014 Increasing anthropogenic nitrogen in the North Pacific Ocean *Sci. Res. Rep.* **346** 1102–5
Kirkby J *et al* 2016 Ion-induced nucleation of pure biogenic particles *Nature* **533** 521
Klimont Z, Smith S J and Cofala J 2013 The last decade of global anthropogenic sulfur dioxide: 2000–2011 emissions *Environ. Res. Lett.* **8** 014003
van Krevelen D W 1950 Graphical–statistical method for the study of structure and reaction processes of coal *Fuel* **29** 269–84
Krishnamurthy A, Moore J K, Mahowald N M, Luo C, Doney S C, Lindsay K and Zender C S 2009 Impacts of increasing anthropogenic soluble iron and nitrogen deposition on ocean biogeochemistry *Glob. Biogeochem. Cycles* **23** GB003440
Krom M D, Kress N, Brenner S and Gordon L I 1991 Phosphorus limitation of primary productivity in the Eastern Mediterranean Sea *Limnol. Oceanogr.* **36** 424–32
Kulmala M *et al* 2004 A new feedback mechanism linking forests, aerosols, and climate *Atmos. Chem. Phys.* **4** 557–62
Kulmala M *et al* 2013 Direct observations of atmospheric aerosol nucleation *Science* **339** 943–6
Lack D A, Langridge J M, Bahreini R, Cappa C D, Middlebrook A M and Schwarz J P 2012 Brown carbon and internal mixing in biomass burning particles *Proc. Natl Acad. Sci. USA* **109** 14802–7
Lamarque J F *et al* 2010 Historical 1850-2000 gridded anthropogenic and biomass burning emissions of reactive gases and aerosols: methodology and application *Atmos. Chem. Phys.* **10** 7017–39
Lamarque J F *et al* 2013 Multi-model mean nitrogen and sulfur deposition from the atmospheric chemistry and climate model intercomparison project (ACCMIP): evaluation of historical and projected future changes *Atmos. Chem. Phys.* **13** 7997–8018
Larsen O and Postma D 2001 Kinetics of reductive bulk dissolution of lepidocrocite, ferrihydrite, and goethite *Geochim. Cosmochim. Acta* **65** 1367–79
Laskin A, Laskin J and Nizkorodov S A 2015 Chemistry of atmospheric brown carbon *Chem. Rev.* **115** 4335–82
LeGrande A N, Tsigaridis K and Bauer S E 2016 Role of atmospheric chemistry in the climate impacts of stratospheric volcanic injections *Nat. Geosci.* **9** 652–5
Lelieveld J and Pöschl U 2017 The air-pollution health crisis *Nat. Commun.* **551** 291–3
Lelieveld J, Evans J S, Fnais M, Giannadaki D and Pozzer A 2015 The contribution of outdoor air pollution sources to premature mortality on a global scale *Nature* **525** 367–71
Lewis E R and Schwartz S E 2004 Sea salt aerosol production: mechanisms, methods, measurements and models—a critical review *Geophys. Monogr. Ser.* **152** 1–413
Lim Y B, Tan Y, Perri M J, Seitzinger S P and Turpin B J 2010 Aqueous chemistry and its role in secondary organic aerosol (SOA) formation *Atmos. Chem. Phys.* **10** 10521–39
Lin G, Sillman S, Penner J E and Ito A 2014 Global modeling of SOA: the use of different mechanisms for aqueous-phase formation *Atmos. Chem. Phys.* **14** 5451–75
Litter M I, Villegas M and Blesa M A 1994 Photodissolution of iron oxides in malonic acid *Can. J. Chem.* **72** 2037–43
Luo C, Mahowald N M, Bond T, Chuang P Y, Artaxo P, Siefert R, Chen Y and Schauer J 2008 Combustion iron distribution and deposition *Glob. Biogeochem. Cycles* **22** GB002964
Mace K A, Kubilay N and Duce R A 2003 Organic nitrogen in rain and aerosol in the eastern Mediterranean atmosphere: an association with atmospheric dust *J. Geophys. Res.* **108** 4320
Mackey K R M and Paytan A 2009 Phosphorus cycle *Encyclopedia of Microbiology* ed M Schaechter (Oxford: Elsevier) pp 322–34
Mahowald N M *et al* 2008 Global distribution of atmospheric phosphorus sources, concentrations and deposition rates, and anthropogenic impacts *Glob. Biogeochem. Cycles* **22** GB003240
Mahowald N M *et al* 2009 Atmospheric iron deposition: global distribution, variability, and human perturbations *Annu. Rev. Mar. Sci.* 245–78
Mahowald N M, Scanza R, Brahney J, Goodale C L, Hess P G, Moore J K and Neff J 2017 Aerosol deposition impacts on land and ocean carbon cycles *Curr. Clim. Change Rep.* **3** 16–31
Mao J, Fan S, Jacob D J and Travis K R 2013 Radical loss in the atmosphere from Cu–Fe redox coupling in aerosols *Atmos. Chem. Phys.* **13** 509–19
Markaki Z, Loye-Pilot M D, Violaki K, Benyahya L and Mihalopoulos N 2010 Variability of atmospheric deposition of dissolved nitrogen and phosphorus in the Mediterranean and possible link to the anomalous seawater N/P ratio *Mar. Chem.* **120** 187–94
Martin J H, Gordon R M and Fitzwater S E 1991 The case for iron *Limnol. Ocean.* **36** 1793–802

McNeill V F 2015 Aqueous organic chemistry in the atmosphere: sources and chemical processing of organic aerosols *Environ. Sci. Technol.* **49** 1237–44

Meskhidze N, Chameides W I, Nenes A and Chen G 2003 Iron mobilization in mineral dust: can anthropogenic $SO_2$ emissions affect ocean productivity? *Geophys. Res. Lett.* **30** GL018035

Meskhidze N, Chameides W L and Nenes A 2005 Dust and pollution: a recipe for enhanced ocean fertilization? *J. Geophys. Res. D Atmos.* **110** D005082

Moore C M *et al* 2013 Processes and patterns of oceanic nutrient limitation *Nat. Geosci.* **6** 701–10

Myriokefalitakis S, Tsigaridis K, Mihalopoulos N, Sciare J, Nenes A, Kawamura K, Segers A and Kanakidou M 2011 In-cloud oxalate formation in the global troposphere: a 3D modeling study *Atmos. Chem. Phys.* **11** 5761–82

Myriokefalitakis S, Daskalakis N, Mihalopoulos N, Baker A R, Nenes A and Kanakidou M 2015 Changes in dissolved iron deposition to the oceans driven by human activity: a 3D global modelling study *Biogeosciences* **12** 3973–92

Myriokefalitakis S, Nenes A, Baker A R, Mihalopoulos N and Kanakidou M 2016 Bioavailable atmospheric phosphorous supply to the global ocean: a 3D global modeling study *Biogeosciences* **13** 6519–43

Myriokefalitakis S *et al* 2017 The contribution of bioaerosols to the organic carbon budget of the atmosphere *Perspectives on Atmospheric Sciences* pp 845–51

Nault B A, Laughner J L, Wooldridge P J, Crounse J D, Dibb J, Diskin G and Cohen R C 2017 Lightning $NO_x$ emissions: reconciling measured and modeled estimates with updated $NO_x$ chemistry *Geophys. Res. Lett.* **44** 9479–88

Neff J C, Holland E A, Dentener F J, McDowell W H and Russell K M 2002 The origin, composition and rates of organic nitrogen deposition: a missing piece of the nitrogen cycle? *Biogeochemistry* **57/58** 99–136

Nenes A, Krom M D, Mihalopoulos N, Van Cappellen P, Shi Z, Bougiatioti A, Zarmpas P and Herut B 2011 Atmospheric acidification of mineral aerosols: a source of bioavailable phosphorus for the oceans *Atmos. Chem. Phys.* **11** 6265–72

Nickovic S, Vukovic A, Vujadinovic M, Djurdjevic V and Pejanovic G 2012 Technical note: high-resolution mineralogical database of dust-productive soils for atmospheric dust modeling *Atmos. Chem. Phys.* **12** 845–55

Nickovic S, Vukovic A and Vujadinovic M 2013 Atmospheric processing of iron carried by mineral dust *Atmos. Chem. Phys.* **13** 9169–81

Oakes M, Ingall E D, Lai B, Shafer M M, Hays M D, Liu Z G, Russell A G and Weber R J 2012 Iron solubility related to particle sulfur content in source emission and ambient fine particles *Environ. Sci. Technol.* **46** 6637–44

Okin G S *et al* 2011 Impacts of atmospheric nutrient deposition on marine productivity: roles of nitrogen, phosphorus, and iron *Glob. Biogeochem. Cycles* **25** GB003858

Olgun N, Duggen S, Langmann B, Hort M, Waythomas C F, Hoffmann L and Croot P 2013 Geochemical evidence of oceanic iron fertilization by the Kasatochi volcanic eruption in 2008 and the potential impacts on Pacific sockeye salmon *Mar. Ecol. Prog. Ser.* **488** 81–8

Ooki A and Uematsu M 2005 Chemical interactions between mineral dust particles and acid gases during Asian dust events *J. Geophys. Res. D Atmos.* **110** D004737

Paris R and Desboeufs K V 2013 Effect of atmospheric organic complexation on iron-bearing dust solubility *Atmos. Chem. Phys.* **13** 4895–905

Paris R, Desboeufs K V and Journet E 2011 Variability of dust iron solubility in atmospheric waters: investigation of the role of oxalate organic complexation *Atmos. Environ.* **45** 6510–7

Pascaud A, Sauvage S, Coddeville P, Nicolas M, Croisé L, Mezdour A and Probst A 2016 Contrasted spatial and long-term trends in precipitation chemistry and deposition fluxes at rural stations in France *Atmos. Environ.* **146** 28–43

Paytan A and McLaughlin K 2007 The oceanic phosphorus cycle *Chem. Rev.* **107** 563–76

Paytan A, Mackey K R M, Chen Y, Lima I D, Doney S C, Mahowald N M, Labiosa R and Post A F 2009 Toxicity of atmospheric aerosols on marine phytoplankton *Proc. Natl Acad. Sci. USA* **106** 4601–5

Pepper I L, Gerba C P and Gentry T J 2015 *Environmental Microbiology* ed I L Pepper, C P Gerba and T J Gentry 3rd edn (New York: Academic)

Perlwitz J P, Pérez García-Pando C and Miller R L 2015 Predicting the mineral composition of dust aerosols—Part 1: representing key processes *Atmos. Chem. Phys.* **15** 11593–627

Pitta P *et al* 2017 Saharan dust deposition effects on the microbial food web in the Eastern Mediterranean: a study based on a mesocosm experiment *Front. Mar. Sci.* **4** 117

Pope III C A and Dockery D W 2013 Air pollution and life expectancy in China and beyond *Proc. Natl Acad. Sci. USA* **110** 12861–2

Pope III C A, Burnett R T, Thun M J, Calle E E, Krewski D and Thurston G D 2002 Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution *J. Am. Med. Assoc.* **287** 1132–41

Pöschl U and Shiraiwa M 2015 Multiphase chemistry at the atmosphere–biosphere interface influencing climate and public health in the Anthropocene *Chem. Rev.* **115** 4440–75

Pozzer A, Tsimpidi A P, Karydis V A, de Meij A and Lelieveld J 2017 Impact of agricultural emission reductions on fine particulate matter and public health *Atmos. Chem. Phys.* **17** 12813–26

Ramanathan V, Crutzen P J, Kiehl J T and Rosenfeld D 2001 Atmosphere aerosols, climate, and the hydrological cycle *Science* **294** 2119–24

Rauch J N and Pacyna J M 2009 Earth's global Ag, Al, Cr, Cu, Fe, Ni, Pb, and Zn cycles *Glob. Biogeochem. Cycles* **23** GB003376

Riccobono F *et al* 2014 Oxidation products of biogenic emissions contribute to nucleation of atmospheric particles *Science* **344** 717–21

Rice E L 1992 Allelopathic effects on nitrogen cycling *Allelopathy: Basic and Applied Aspects* ed V Rizvi (Dordrecht: Springer) pp 31–58

Richon C *et al* 2017 Modeling the impacts of atmospheric deposition of nitrogen and desert dust-derived phosphorus on nutrients and biological budgets of the Mediterranean Sea *Prog. Oceanogr.* (https://doi.org/10.1016/j.pocean.2017.04.009)

Rossignol S, Aregahegn K Z, Tinel L, Fine L, Nozière B and George C 2014 Glyoxal induced atmospheric photosensitized chemistry leading to organic aerosol growth *Environ. Sci. Technol.* **48** 3218–27

Rudich Y 2003 Laboratory perspectives on the chemical transformations of organic matter in atmospheric particles *Chem. Rev.* **103** 5097–124

Schlesinger W H 1977 Carbon balance in terrestrial detritus *Annu. Rev. Ecol. Syst.* **8** 51–81

Schroth A W, Crusius J, Sholkovitz E R and Bostick B C 2009 Iron solubility driven by speciation in dust sources to the ocean *Nat. Geosci.* **2** 337–40

Sedlak D L, Hoignk J, David M M, Colvile R O Y N, Seyffer E, Acker K, Wiepercht W, Lindii J A and Fuzzi S 1997 The cloudwater chemistry of iron and copper at Great Dun Fell, UK *Atmos. Environ.* **31** 2515–26

Sedwick P N, Sholkovitz E R and Church T M 2007 Impact of anthropogenic combustion emissions on the fractional solubility of aerosol iron: evidence from the Sargasso Sea *Geochem. Geophys. Geosyst.* **8** 1–21

Seinfeld J H and Pandis S N 2006 *Atmospheric Chemistry and Physics: from Air Pollution to Climate Change* 2nd edn (Oxford: Wiley)

Shi Z *et al* 2011a Influence of chemical weathering and aging of iron oxides on the potential iron solubility of Saharan dust during simulated atmospheric processing *Glob. Biogeochem. Cycles* **25** GB2010

Shi Z, Bonneville S, Krom M D, Carslaw K S, Jickells T D, Baker A R and Benning L G 2011b Iron dissolution kinetics of mineral dust at low pH during simulated atmospheric processing *Atmos. Chem. Phys.* **11** 995–1007

Shi Z, Krom M D, Jickells T D, Bonneville S, Carslaw K S, Mihalopoulos N, Baker A R and Benning L G 2012 Impacts on iron solubility in the mineral dust by processes in the source region and the atmosphere: a review *Aeolian Res.* **5** 21–42

Sholkovitz E R, Sedwick P N, Church T M, Baker A R and Powell C F 2012 Fractional solubility of aerosol iron: synthesis of a global-scale data set *Geochim. Cosmochim. Acta* **89** 173–89

Shrivastava M *et al* 2017 2017 Recent advances in understanding secondary organic aerosol: implications for global climate forcing *Rev. Geophys.* **55** 509–59

Sigee D C 2005 Uptake of nitrate and ammonium ions by algae *Freshwater Microbiology: Biodiversity and Dynamic Interactions of Microorganisms in the Aquatic Environment* (New York: Wiley) pp 257–60

Smil V 2000 Phosphorus in the environment: natural flows and human interferences *Annu. Rev. Energy Environ.* **25** 53–88

Spracklen D V *et al* 2011 Aerosol mass spectrometer constraint on the global secondary organic aerosol budget *Atmos. Chem. Phys.* **11** 12109–36

Stevens B and Feingold G 2009 Untangling aerosol effects on clouds and precipitation in a buffered system *Nature* **461** 607–13

Stockdale A, Krom M D, Mortimer R J G, Benning L G, Carslaw K S, Herbert R J, Shi Z, Myriokefalitakis S, Kanakidou M and Nenes A 2016 Understanding the nature of atmospheric acid processing of mineral dusts in supplying bioavailable phosphorus to the oceans *Proc. Natl Acad. Sci. USA* **113** 14639–44

Suntharalingam P, Buitenhuis E, Le Quéré C, Dentener F, Nevison C, Butler J H, Bange H W and Forster G 2012 Quantifying the impact of anthropogenic nitrogen deposition on oceanic nitrous oxide *Geophys. Res. Lett.* **39** GL050778

Surratt J D *et al* 2007 Evidence for organosulfates in secondary organic aerosol *Environ. Sci. Technol.* **41** 517–27

Surratt J D, Chan A W H, Eddingsaas N C, Chan M, Loza C L, Kwan A J, Hersey S P, Flagan R C, Wennberg P O and Seinfeld J H 2010 Reactive intermediates revealed in secondary organic aerosol formation from isoprene *Proc. Natl Acad. Sci. USA* **107** 6640–5

Tagliabue A, Bowie A R, Boyd P W, Buck K N, Johnson K S and Saito M A 2017 The integral role of iron in ocean biogeochemistry *Nature* **543** 51–9

Textor C *et al* 2006 Analysis and quantification of the diversities of aerosol life cycles within AeroCom *Atmos. Chem. Phys.* **6** 1777–813

Theodosi C, Markaki Z and Mihalopoulos N 2010 Iron speciation, solubility and temporal variability in wet and dry deposition in the Eastern Mediterranean *Mar. Chem.* **120** 100–7

Tipping E *et al* 2014 Atmospheric deposition of phosphorus to land and freshwater *Environ. Sci. Process. Impacts* **16** 1608–17

Tsigaridis K and Kanakidou M 2007 Secondary organic aerosol importance in the future atmosphere *Atmos. Environ.* **41** 4682–92

Tsigaridis K *et al* 2014 The AeroCom evaluation and intercomparison of organic aerosol in global models *Atmos. Chem. Phys.* **14** 10845–95

Twining B S, Fisher N S, Baines S B and Fisher N S 2004 Element stoichiometries of individual plankton cells collected during the Southern Ocean iron experiment (SOFeX) *Limnol. Ocean.* **49** 2115–28

Twining B S and Baines S B 2013 The trace metal composition of marine phytoplankton *Annu. Rev. Mar. Sci.* **5** 191–215

Uematsu M, Toratani M, Kajino M, Narita Y, Senga Y and Kimoto T 2004 Enhancement of primary productivity in the western North Pacific caused by the eruption of the Miyake-jima Volcano *Geophys. Res. Lett.* **31** L06106

Usher C R, Michel A E and Grassian V H 2003 Reactions on mineral dust *Chem. Rev.* **103** 4883–940

Vet R *et al* 2014 A global assessment of precipitation chemistry and deposition of sulfur, nitrogen, sea salt, base cations, organic acids, acidity and pH, and phosphorus *Atmos. Environ.* **93** 3–100

Vinken G C M, Boersma K F, Maasakkers J D, Adon M and Martin R V 2014 Worldwide biogenic soil $NO_x$ emissions inferred from OMI $NO_2$ observations *Atmos. Chem. Phys.* **14** 10363–81

Volkamer R, Ziemann P J and Molina M J 2009 Secondary organic aerosol formation from acetylene: seed effect on SOA yields due to organic photochemistry in the aerosol aqueous phase *Atmos. Chem. Phys.* **9** 1907–28

van Vuuren D P *et al* 2011 The representative concentration pathways: an overview *Clim. Change* **109** 5–31

Wang G H, Zhou B H, Cheng C L, Cao J J, Li J J, Meng J J, Tao J, Zhang R J and Fu P Q 2013 Impact of Gobi Desert dust on aerosol chemistry of Xi'an, inland China during spring 2009: differences in composition and size distribution between the urban ground surface and the mountain atmosphere *Atmos. Chem. Phys.* **13** 819–35

Wang L, Khalizov A F, Zheng J, Xu W, Ma Y, Lal V and Zhang R 2010 Atmospheric nanoparticles formed from heterogeneous reactions of organics *Nat. Geosci.* **3** 238–42

Wang R, Balkanski Y, Boucher O, Ciais P, Peñuelas J and Tao S 2014 Significant contribution of combustion-related emissions to the atmospheric phosphorus budget *Nat. Geosci.* **8** 48–54

Wang R *et al* 2015a Anthropogenic aerosol deposition reduces the sensitivity of oceanic productivity to warming *Geophys. Res. Lett.* **42** 745–10

Wang R, Balkanski Y, Boucher O, Bopp L, Chappell A, Ciais P, Hauglustaine D, Peñuelas J and Tao S 2015b Sources, transport and deposition of iron in the global atmosphere *Atmos. Chem. Phys.* **15** 6247–70

Warneck P 2005 Multi-phase chemistry of C2 and C3 organic compounds in the marine atmosphere *J. Atmos. Chem.* **51** 119–59

Watmough S A, Eimers C and Baker S 2016 Impediments to recovery from acid deposition *Atmos. Environ.* **146** 15–27

Waxman E M, Dzepina K, Ervens B, Lee-Taylor J, Aumont B, Jimenez J L, Madronich S and Volkamer R 2013 Secondary organic aerosol formation from semi- and intermediate-volatility organic compounds and glyoxal: relevance of O/C as a tracer for aqueous multiphase chemistry *Geophys. Res. Lett.* **40** 978–82

Weber R J, Guo H, Russell A G and Nenes A 2016 High aerosol acidity despite declining atmospheric sulfate concentrations over the past 15 years *Nat. Geosci.* **9** 282–5

Wilson T W *et al* 2015 A marine biogenic source of atmospheric ice-nucleating particles *Nature* **525** 234–8

Xu L, Suresh S, Guo H, Weber R J and Ng N L 2015a Aerosol characterization over the southeastern United States using high-resolution aerosol mass spectrometry: spatial and seasonal variation of aerosol composition and sources with a focus on organic nitrates *Atmos. Chem. Phys.* **15** 7307–36

Xu L *et al* 2015b Effects of anthropogenic emissions on aerosol formation from isoprene and monoterpenes in the southeastern United States *Proc. Natl Acad. Sci. USA* **112** 37–42

Zamora L M, Landolfi A, Oschlies A, Hansell D A, Dietze H and Dentener F 2010 Atmospheric deposition of nutrients and excess N formation in the North Atlantic *Biogeosciences* **7** 777–93

Zhang R, Khalizov A, Wang L, Hu M and Xu W 2012 Nucleation and growth of nanoparticles in the atmosphere *Chem. Rev.* **112** 1957–2011

Zhang Y *et al* 2017 Top-of-atmosphere radiative forcing affected by brown carbon in the upper troposphere *Nat. Geosci.* **10** 486–9