Science of the Total Environment 468–469 (2014) 265–271

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Chemical interaction of atmospheric mineral dust-derived nanoparticles with natural seawater — EPS and sunlight-mediated changes

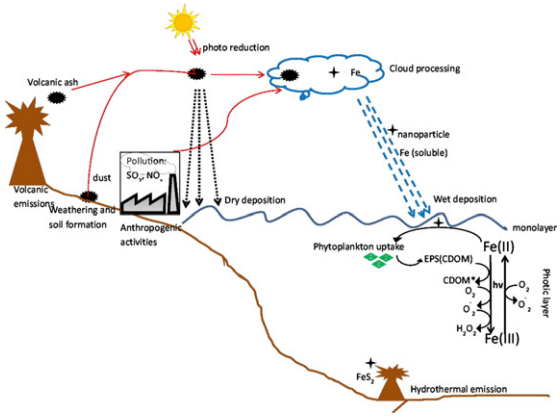
Enikö Kadar [a,*], Michael Cunliffe [b], Andrew Fisher [c], Björn Stolpe [d], Jamie Lead [d,e], Zongbo Shi [d]

[a] Plymouth Marine Laboratory, Prospect Place, the Hoe, Plymouth PL1 3DH, UK
[b] Marine Biological Association of the United Kingdom, The Laboratory, Plymouth PL1 2PB, UK
[c] School of Geography, Earth and Environmental Sciences, University of Plymouth, Drake Circus, Plymouth PL4 8AA, UK
[d] School of Geography, Earth and Environmental Sciences, University of Birmingham, B15 2TT UK
[e] SmartState Center for Environmental Nanoscience and Risk (CENR), Department of Environmental Health Sciences, Arnold School of Public Health, University of South Carolina, SC 29028 USA

HIGHLIGHTS

- Nanomaterials from simulated cloud processing of dusts were interacted with seawater.
- Aggregation is more polydisperse and unstable in seawater than in MQ water.
- Microalgal exopolymeric substances (EPSs) stabilises dust derived NP aggregates.
- EPS enhances Fe dissolution from NPs, and this is enhanced in the absence of light.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 July 2013
Received in revised form 16 August 2013
Accepted 17 August 2013
Available online 10 September 2013

Editor: Damia Barcelo

Keywords:
Iron oxide nanoparticle
Aggregation
Dissolution
Bioavailability
EPS

ABSTRACT

Laboratory studies were conducted to investigate the interactions of nanoparticles (NPs) formed via simulated cloud processing of mineral dust with seawater under environmentally relevant conditions. The effect of sunlight and the presence of exopolymeric substances (EPS) were assessed on the: (1) colloidal stability of the nanoparticle aggregates (i.e. size distribution, zeta potential, polydispersity); (2) micromorphology and (3) Fe dissolution from particles. We have demonstrated that: (i) synthetic nano-ferrihydrite has distinct aggregation behaviour from NPs formed from mineral dusts in that the average hydrodynamic diameter remained unaltered upon dispersion in seawater (~1500 nm), whilst all dust derived NPs increased about three fold in aggregate size; (ii) relatively stable and monodisperse aggregates of NPs formed during simulated cloud processing of mineral dust become more polydisperse and unstable in contact with seawater; (iii) EPS forms stable aggregates with both the ferrihydrite and the dust derived NPs whose hydrodynamic diameter remains unchanged in seawater over 24 h; (iv) dissolved Fe concentration from NPs, measured here as <3 kDa filter-fraction, is consistently >30% higher in seawater in the presence of EPS and the effect is even more pronounced in the absence of light; (v) micromorphology of nanoparticles from mineral dusts closely resemble that of synthetic ferrihydrite in MQ water, but in seawater with EPS

* Corresponding author. Tel.: +44 1752 633450 (direct); fax: +44 1752 633101.
E-mail address: enik@pml.ac.uk (E. Kadar).
URL: http://www.pml.ac.uk (E. Kadar).

http://dx.doi.org/10.1016/j.scitotenv.2013.08.059

they form less compact aggregates, highly variable in size, possibly due to EPS-mediated steric and electrostatic interactions. The larger scale implications on real systems of the EPS solubilising effect on Fe and other metals with the additional enhancement of colloidal stability of the resulting aggregates are discussed.

1. Introduction

Atmospheric chemical processes that occur in clouds generate iron rich nanoparticles (NPs) from mineral dusts (Kadar et al., 2013). Nano-iron has been suggested to be a major portion of the bioavailable fraction of the metal (Raiswell et al., 2008). However, before becoming available for biological uptake by marine phytoplankton, NPs originated from cloud mediated processes undergo rapid transformations (such as aggregation, photo-reduction, dissolution and interaction with natural organic matter) immediately in contact with seawater. These reactions are too fast to be easily monitored in the field and therefore require real time analyses and experimentation under carefully controlled laboratory conditions (Shi et al., 2010). Thus we have conducted laboratory studies to investigate how the simulated cloud-derived Fe-rich nanoparticles interact with natural oceanic seawater and how their composition, size, surface topology and chemical reactivity change under a range of environmental conditions.

Exo-polymeric substances (EPSs) secreted by phytoplankton constitute a large and dynamic pool of oceanic dissolved organic carbon (DOC) (Engel et al., 2004; Fogg, 1983) with key roles in the formation of marine biofilms and in colloid and trace element scavenging (Fogg, 1983; Myklestad, 1995). About half of the global photosynthetic activity is performed by phytoplankton (Chisholm, 2000) and ~40–60% of the resulting biomass is released as EPS suggesting its crucial importance in the global carbon cycling and potential driving force in sequestration of atmospheric CO_2. In addition, changes in the EPS assembly kinetics were recently reported to be induced by engineered NPs (Chen et al., 2011) suggesting a potential disturbance to the marine carbon cycle. This ecological impact of synthetic NPs draws attention to the importance of interactions between EPS–nanoparticles. Furthermore, our recent study (Kadar et al., 2012) revealed improved metabolic parameters in some marine microalgae cultured on synthetic nano-iron enriched media and the uptake mechanisms involved secretion of EPS. The same study showed that synthetic nano-iron was preferred over EDTA–Fe used in laboratory cultures in generic growth media suggesting that the nanoparticulate form of the metal may be more bioavailable to microalgae. Whilst originally the term EPS stands for "extracellular polysaccharides", it is now acknowledged that these matrixes are more complex, including lipopolysaccharides, glycolipids, lipids, proteins or peptides and nucleic acids. Interaction of the atmospheric dust-derived "natural nanoparticles" with EPS could therefore be a complex key factor influencing bioavailability of iron, and although we have started to understand how marine algae might take up nano forms of the metal (Kadar et al., 2012) we do not fully understand the influence of seawater EPS on the environmental fate of (nano)particles.

Here we used an EPS extract from a common phytoplankton species – *Nannochloropsis salina* – and added to natural oceanic seawater in order to investigate the physicochemical transformations of atmospheric dust-derived "natural Fe-rich nanoparticles" in contact with seawater so that we can better understand their environmental fate and behaviour.

This is a follow up study (part I focused on NP formation via simulated cloud processing of mineral dusts with distinct Fe-content), which investigates the possible transformations that take place when dust-derived particles come in contact with seawater. Specifically, here we have studied the composition, Fe dissolution/Fe lability, particle aggregation/size distribution, surface topology and zeta potential, i.e. colloidal stability of the dust derived NPs, both immediately and 24 h after coming in contact with seawater under a range of environmentally realistic conditions (i.e. typical in oceanic waters, in the presence of EPS particles and under distinct photo-oxidative conditions). To the best of our knowledge, this is the first research attempting to systematically investigate the changes in physico chemical properties of Fe-rich environmental NPs upon dispersion in seawater with and without EPS, which shed new light on the environmental fate and behaviour of natural NPs derived from atmospheric aerosols.

2. Experimental

2.1. Dust samples

Three dust models including (a) Sahara desert, Morocco (30°16′ N-4°55′W); (b) Libya (25°35′N-16°31′E) and (c) volcanic ash (unweathered lapilli collected after eruption of Etna in July 2011; 37°44′N-14°59′E) were exposed to simulated cloud processing following previously reported protocol (Kadar et al., 2013).

2.2. EPS extraction from phytoplankton culture and quantification

Exopolymer particles were extracted by cross-flow ultrafiltration according to the method reported by Zhang and Santschi (2009), from a 20 L stationary culture of *N. salina* (CCAP 849/3) grown in a 450 L photo bioreactor to a density of 16×10^6 cells mL^{-1}. Culture conditions were: 20 °C; 16/8 light/dark regime; f/2 medium dissolved in Instant Ocean®. The phytoplankton culture was centrifuged at 4000 rpm for 30 min and the supernatant was collected for free dissolved EPS following the previously reported method (Zhang and Santschi, 2009). Briefly, 20 L supernatant fraction was filtered (<0.45 μm) and ultra-filtered on a 1 kDa cartridge (GE Healthcare UK) to ~300 mL retentate. The cartridge was rinsed with 200 mL MQ water, and then soaked for 6 h following washing with 200 mL MQ twice. The first retentate, the rinse and the two washing solutions were combined resulting in 1 L EPS extract which was used in subsequent experimentations as described below. The transparent exopolymeric substance (TEP) fraction of the EPS, operationally defined as Alcian Blue staining particles greater than 0.2, was quantified (Cunliffe et al., 2009) as the xantham gum equivalents and was 4.66 $mg \cdot L^{-1} \pm 0.81$, which converted to carbon gives 2.94 mg C $L^{-1} \pm 0.51$. These are typical concentrations in very productive waters, such as estuaries and thus a 1:20 (v/v) addition of this stock EPS to oceanic, 30 kDa-filtered seawater is an environmentally realistic dose.

2.3. Nanoparticle–seawater interactions

Nanoparticles were obtained via the previously described cloud simulation protocol (Kadar et al., 2013) using 30 mg dust powder in 500 mL of 0.1 N H_2SO_4 solution (pH 1) stirred (120 rot. min^{-1}) for 96 h followed by a drop-wise neutralisation (to pH ~ 6) using concentrated NaOH solution (Sigma). Samples and standards were prepared in HDPE tubes. All equipment had been carefully acid washed prior to use. All reagents were from Sigma Aldrich and at least p.a. grade. All solutions were prepared in MQ water (Millipore). The dust suspensions at pH ~ 6 (which contain Fe-rich NPs) were then pre-filtered on 0.45 μ pore size membranes to remove insoluble material before addition to natural seawater (1:10) from the L4 station of the Western Channel Observatory of PML (50°15′N-4°13′W) with well characterised physico-chemistry (http://www.westernchannelobservatory.org.uk/data.php).