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Comments on 'Influence of measurement uncertainties on fractional solubility of iron in mineral aerosols over the oceans' Aeolian Research 22, 85-92.

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Meskhidze et al. (Aeolian Research, 22, 85-92) provide a timely reminder of uncertainties in measuring the fractional solubility of iron in mineral dust, which are a major source of uncertainty in modelling the delivery of iron to the oceans (Tagliabue et al., 2016). The main focus of their paper is the errors that occur during the determination of fractional solubility (using distilled water or DI leaches) due to the dissolution of <0.45 µm particles during storage of the leaches. We agree that such dissolution errors are important, but go further here in choosing to emphasise the fundamental role of mineralogy, which lies at the heart of the errors in this methodology. Our view is that DI leach errors need to be considered in relation to the forms of iron in dust samples and their mineralogical associations.

The DI technique leaches dust at pH 5.6 through a <0.45 µm filter in a flow through system (Buck et al., 2006; 2010). This minimises Fe losses due to precipitation of $Fe(OH)_3$ and thus provides consistent and reproducible results. The leach is acidified to pH 1.7 and stored prior to analysis. No studies have been made of the nature of the Fe extracted by the DI leach but Meskhidze et al. (2016) believe the leach includes Fe-rich nanoparticles (mineralogy unspecified), iron in crystalline (oxyhydr)oxides and iron in aluminosilicate minerals. These forms of iron may range in size from nanoparticles (<0.1 µm) through to colloids (0.1 to 1.0 µm) and may be associated with surfaces, or may occur as discrete grains or as aggregates (with little or no organic matter; Raiswell and Canfield, 2012). All these forms are solid phases with mineral characteristics. The <0.45 µm DI leach represents a similar size fraction as is commonly used for estimating 'dissolved' Fe (dFe) in seawater although Meskhidze et al. (2016) point out that dFe in seawater differs from the DI leach in consisting mainly of nanoparticulate and colloidal aggregates closely associated with organic matter (see also Boye et al., 2010). The form of the iron in dFe probably consists of ionic species complexed to organic ligands and iron (oxyhydr)oxides aggregated and/or complexed with organic matter (Mackey and Zirino, 1994).

Meskhidze et al. (2016) suggest that the reproducibility of the DI leach make it a suitable candidate for a standard leach protocol but identify two errors. The first arises from the continued dissolution of <0.45 µm poorly soluble particles during storage at pH 1.7. Analysis immediately after filtration would minimise this problem. Alternatively a portion of the <0.45 DI leach filtered immediately through a 0.02 µm filter (e.g., a Whatman Anotop syringe filter) would produce a filtrate consisting predominantly of aqueous species (not strictly correct but a reasonable pragmatic assumption; see Raiswell and Canfield, 2012; Shiller, 2003). The 0.02-0.45 µm fraction collected on the filter could be studied by direct observation (see below) and compared to a sub-sample of the same leach examined after storage at pH 1.7. Any significant dissolution during storage will produce observable differences between the two samples. A second source of error arises from the dissolution of a <0.45 µm fraction produced where wetting disaggregates dust grains. Some disaggregation may usefully mitigate the effects of compaction during filtration but clearly filtration artefacts also need to be studied from a mineralogical perspective.

Identifying and quantifying the mineralogy of Fe in the 0.02-0.45 µm fraction can only be addressed by the direct observation of individual mineral grains. Shi et al. (2012) have reviewed the most common direct observation techniques. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) associated with EDX (energy dispersive X-ray spectrometry) provide element composition, size and morphological data down to nanometer scales. TEM together with selective area X-ray diffraction (SAED) provide mineralogical data. Recent applications of these techniques have been published by Kadar et al. (2014), Jeong and Achterberg (2014) and Baddock et al. (2013). Synchrotron-based X-ray absorption spectroscopy can also be used to identify iron speciation (von der Heyden et al., 2012; Oakes et al., 2013). All these techniques are suitable for use with the small weights (<0.1 mg) typical of aeolian mineral dust samples.

The dust literature uses a wide variety of methodologies that have produced fractional solubilities ranging from 0.001-80% (Baker and Croot, 2010). Modelling studies generally use values toward the lower end of the this range. For example Tagliabue et al. (2009) assumed a fractional solubility of 0.5% with continued slower dissolution occurring at a rate of 0.0002% per day. Lancelot et al. (2009) assumed a fractional solubility of 2%, Boyd et al. (2012) used fractional solubilities varying from 1-10% and Death et al. (2014) assumed fractional solubility of 2%. Boyd et al. (2010) point out that there is little justification for these arbitrary choices for fractional solubility although Raiswell et al. (2016) have estimated a fractional solubility of ~ 1% for the dissolution of ascorbic acid soluble Fe from mineral dust (see below).

Mineralogy can also provide important constrains on the fractional solubility determinations by different methodologies. Unfortunately most dust extraction methodologies provide only qualitative statements on mineral extraction that suggest there is considerable variability in extraction behaviour with respect to different iron minerals (Raiswell et al., 2016). For example, Baker et al. (2006) use a pH 4.7 ammonium acetate extraction which dissolves negligible concentrations of Fe (oxyhydr)oxides (see Poulton and Canfield, 2005); Chen and Siefert (2003) use pH 4.5 formate-acetate extraction which was stated to dissolve Fe (oxyhydr)oxides (mineralogy unspecified) and Berger et al. (2008) use a pH 2 hydroxylamine hydrochloride extraction which Winton et al. (2015) report as dissolving metals from biogenic material, adsorbed to clay minerals and present as Fe and Mn (oxyhydr)oxides. Raiswell et al. (2016) use an ascorbic acid extraction that is highly selective for fresh ferrihydrite (also known as hydrous ferric oxide or HFO) and which dissolves negligible concentrations of iron from aged ferrihydrite, lepidocrocite, goethite, hematite and aluminosilicate minerals. The adoption of a standard methodology thoroughly calibrated against minerals commonly present in dusts would diminish the between-sample variation in fractional solubility.

Mineralogy may also provide important insights into potential bioavailability (Raiswell et al., 2016). Most dFe is considered to be bioavailable because organically bound Fe can be taken up by phytoplankton through several known pathways (Shaked and Lis, 2012; Meskhidze et al.,2016). However the iron dissolved by the DI leach is mainly inorganic (see above) and only the highly reactive and/or amorphous phases are likely to be bioavailable. For example there is experimental evidence to suggest that poorly crystalline or amorphous phases such as ferrihydrite can be used by plankton (Wells et al., 1983; Rich and

Morel, 1990; Kuma and Matsunga, 1995; Nodwell and Price, 2001). By contrast the more crystalline phases may not be readily bioavailable unless modified by dissolution or grazing (Barbeau et al., 1996; Shaked and Lis, 2012). Thus using a technique that extracts only adsorbed or amorphous iron phases (such as ferrihydrite), and excludes contributions from crystalline phases would produce a closer correspondence between dFe and the DI leach.

Iron mineralogy has often been peripheral to the dust research agenda although it plays a crucial role in atmospheric processes such as radiative forcing and ice nucleation (Mahowald, 2013). Unfortunately observations of dust iron minerals are scarce although models such as those presented by Scanza et al.(2015), Perlwitz et al.(2015) and Journet et al.(2014) are now trying explicitly to represent dust mineralogy and their impacts on the climate system. Here we argue that an improved focus on the occurrence, properties and extraction behaviour of dust iron (oxyhydr)oxides would provide valuable insights into the potential bioavailability of iron, and clarify its role in ocean biogeochemistry modelling. From a modelling perspective it would also be extremely valuable for validation purposes if leaches were carried out on a variety of size-resolved dusts and minerals, along the lines depicted above.

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