

## Aquatic hydrous iron oxide colloids: evidencing the ambiguities

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Aquatic hydrous iron oxide particles are recognised as ubiquitous carriers of trace elements (1). Usually,  $Fe_{part}$  is determined following operationally defined analytical schemes providing only averaged information of the bulk sample that mask the detailed nature of individual particles. Additionally, prediction of their sorptive properties relies on thermodynamic considerations and conceptual views of the surface-water interface (2). These models are calibrated using well characterised synthetic iron oxides that usually bear little resemblance to natural colloids. The knowledge of the physicochemical characteristics of aquatic iron-rich colloids at the scale of individual particles is thus compulsory to understand and predict their role in the fate of contaminants. We present observations of the morphology, chemical composition and evolution of iron-rich particles in several aquatic environments to demonstrate that conventional notions of iron-organic interactions need to be revised.

Hydrous iron oxide particles are produced at oxic-anoxic interfaces and are depicted as poorly crystallised globules with natural organic matter (NOM) coatings which affect their surface charge and adsorption behaviour. Ill-characterised macromolecular organic matter is usually not taken into account in the genesis of  $Fe_{part}$ . However, interactions between colloidal organic matter and iron-rich globules may lead to bridged entities with modified coagulation/sedimentation properties. Alternatively, organic matter may catalyse electron transfers during oxidation of  $Fe^{2+}$ , leading to blended organic-iron particles with specific surface reactivities. Additionally, the inclusion of foreign ions into the iron phase during particle formation modifies certainly their reactivity.

Our microscopic observations show that macromolecular NOM is systematically involved in the

production and trapping of hydrous iron oxides. This is evidenced by results of field studies in distinct environments presenting a redox interface: Lake Lugano (CH; 3), Paul Lake (USA; 4), and a drained peatland in the Vallée des Ponts crossed by the Bied River (CH; 5).

Transmission electron microscopy (TEM) of specimens from the Fe-rich layers of Lake Lugano, Paul Lake and from the Bied River reveals different morphotypes. Elemental analyses by energy dispersive spectrometry (TEM-EDS) confirmed that these particles almost exclusively contain iron, their intimate composition differing from site to site. In Lake Lugano, miniature granules (diameter *c.* 10–50 nm) are embedded in networks of fibrillar organic matter connected to their parent bacteria. In Paul Lake, inter-connected organic fibrils are rendered electron-dense by a natural iron stain and form a material that is morphologically ill-defined. In the Bied River, large (100–500 nm) particles appear as asymmetric drop-like globules or spheres. At each site, Fe-rich particles contain non-negligible amounts of P (Lugano: P:Fe ~ 0.5), Ca (Bied: Ca:Fe ~ 0.3) or Si (Paul: Si:Fe ~ 0.2), and other elements (Al, S, Cl).

In both lakes, photosynthesis produces aquagenic NOM such as extracellular polymeric substances (EPS). The omnipresence of EPS was unequivocally assessed with a highly selective Ag-protein stain for neutral/acidic polysaccharides. TEM examination of labelled specimens revealed polysaccharides ranging from large fibres to ultrathin (< 5 nm) networked fibrils, confirming the dominant aquagenic origin of lacustrine NOM. In the Vallée des Ponts, NOM has a pedogenic origin. The conformation of this humic/fulvic material varies with concentration, pH and ionic strength (Is). In our case, humics identified as granular material in peat samples act as nucleation sites for the oxidation of  $Fe^{2+}$  when oxic

conditions raise from drains to the river. This was confirmed by elemental mapping (STEM-EDS) of the resulting riverine particles, showing a depletion of iron and calcium in their inner core, and by electron energy loss spectrometry (TEM-EELS), revealing a carbon-rich core.

In the three cases, factors governing  $Fe_{part}$  morphotypes are (i) the concentration of total ions,  $[Fe]_{tot}$  and  $[NOM]$ , and (ii) the nature of the predominant form of NOM. In the Fe-rich peak of Lake Lugano Is ~ 5 mM,  $[Fe]_{tot}$  < 0.5  $\mu$ M, TOC ~ 100  $\mu$ M C; in Paul Lake Is < 0.4 mM,  $[Fe]_{tot}$  ~ 100  $\mu$ M, TOC ~ 350  $\mu$ M C, while in the Bied River Is ~ 0.5 mM,  $[Fe]_{tot}$  ~ 20  $\mu$ M, TOC > 1.5 mM C. For lacustrine conditions, a low  $[Fe]_{tot}$ :TOC ratio (Lake Lugano) favours the growth of distant Fe-rich nanogranules onto fibrillar networks; this process does not modify the morphology of existing EPS fibrils remaining mostly attached to their bacteria. A higher  $[Fe]_{tot}$ :TOC ratio in a low Is medium (Paul Lake) favours coordination of  $Fe^{2+}$  by the chelating groups of NOM (as compared to other cations), leading to  $Fe^{2+}$ -saturated oxidation/nucleation sites. This coating modifies the structure of NOM and produces ill-defined Fe-rich entities onto collapsed polysaccharide fibrils. The systematic association of iron to EPS suggests a catalytic effect of fibrillar organic matter on the formation of intimate Fe-polysaccharides entities. In contrast, granular humic material (Vallée des Ponts) directly catalyses the oxidation of  $Fe^{2+}$  to generate a thick iron-rich surface coating. The nature of the dominant organic matter (aquagenic vs pedogenic) thus directly influences the morphology of the resulting Fe-NOM-rich colloids.

Differences in the observed morphotypes of Fe-rich particles raise important questions on their transport dynamics through water masses. If one relies on classical coagulation theories, one predicts efficient collisions between submicrometer colloids leading to larger, fast-sedimenting entities. Our observations suggest that this process is strongly hampered for colloids imprisoned in fibrillar networks limiting collision efficiency. In addition, highly hydrated polysaccharides will confer a low density to the resulting Fe-EPS entities, thus reducing their sedimentation rate. Eventually, the morphology of  $Fe_{part}$  is influenced by hydrodynamic drag forces: this is exemplified by the drop-like morphology of riverine Fe-rich particles forming under directional hydraulic flow.

Our results also show that Fe-NOM-rich particles are far from pure hydrous iron oxides, because they contain large proportions of other elements. The amount of Si within particles is highly variable at

each site, but the constant  $[P]:[Fe]$  ratio in Lake Lugano suggests the formation of a stoichiometric phase (3), while the relatively constant  $[Ca]:[Fe]$  ratio in the Bied River suggests a simultaneous entrainment of iron and calcium during accretion of humic-rich granules (5). The effect of impurities on the reactivity of Fe-rich particles is not well documented; nevertheless, the presence of foreign ions in the matrix of Fe-NOM particles may induce contrasting interactions with trace elements. For instance, preliminary results suggest that Fe-NOM-rich entities in Paul Lake are selective carriers of Pb (4).

To conclude, hydrous iron oxides systematically present specific morphotypes that are always associated with NOM. Different types of NOM exert different effects on the production of  $Fe_{part}$ . These entities contain large proportions of foreign ions, their presence likely affecting the reactivity of the iron oxides, while the morphology of particles influences their transport behaviour. Consequently, it is misleading to consider aquatic hydrous iron oxide colloids as a well defined chemical species. Speciation models, primarily parametrised for pure iron oxides, do not predict accurately the particle/solution partition. Our observations thus open new opportunities for understanding the role of iron particles in the scavenging of trace elements and should force the existing paradigm of the iron particle as a pure mineral phase towards more realistic considerations.

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### References

1. Davison, W. and Devitre, R.R. (1992) In: *Environmental Particles I* (eds. Buffle, J. and van Leeuwen, H.P.), 315-355. Lewis, Chelsea.
2. Stumm, W. (1995) In: *Aquatic Chemistry: Interfacial and Interspecies Processes* (eds. Huang, C.P., O'Melia, C.R. and Morgan, J.J.), 1-32. ACS, New York.
3. Lienemann, C.-P., Monnerat, M., Dominik, J. and Perret, D. (1998). *Aquat. Sci.* accepted for publication.
4. Taillefert, M., Lienemann, C.-P., Gaillard, J.-F. and Perret, D. (1998) In preparation.
5. Couture, C., Mavrocordatos, D., Atteia, O. and Perret, D. (1998) *Phys. Chem Earth* in press.