

Background & theory - GIS mapping of Eocene sand horizons and iron contamination in streams in the Thames Basin, west of London

Contacts:

Dr. A.W.L. Dudeney

Honorary Reader in Process
Technology
Centre for Environmental Policy
Imperial College London
Prince Consort Road,
London SW7 2AZ
T: 07745 161228
E: a.dudeney@imperial.ac.uk

Dr Philippa J. Mason

Lecturer in Remote Sensing & GIS
Department of Earth Science &
Engineering
Imperial College London
Prince Consort Road,
London SW7 2AZ,
T: +44 (0)20 7594 6528;
E: p.j.mason@imperial.ac.uk

Ms J. Barrott

PhD Student
Department of Earth Sciences,
South Parks Road,
Oxford OX1 3AN
T: 01865 272001
E: julia.barrott@univ.ox.ac.uk

The Tertiary sedimentary structure of South East England includes significant sand deposits of Eocene age (44-50 Ma) occurring mainly in the Thames Valley and Hampshire Basin. Within an area of some 600 km² to the west of London (the area covered by the map), such deposits, nowadays referred to as the Bracklesham Group (Ellison & Williamson, 1999), occur predominantly as low hills (25-180 m AOD) resting on gently folded London Clay (50-55 Ma) and underlying Cretaceous chalk (>65 Ma). In this area, the Bracklesham Group (thickness <110 m) is comprised of three main sand horizons separated by minor clay-rich and/or gravel-rich layers:

- Camberley Sand Formation (uppermost, thickness <70 m);
- Windlesham Sand Formation (intermediate, thickness <20 m); and,
- Bagshot Sand Formation (lowest, thickness <40 m).

The sands are considered to be remnants of original structures left in place after erosion since the last ice age (0.01 Ma), the ice sheet reaching just to the north of the present day Thames. They are now partly obscured by Quaternary river terraces and alluvium, primarily as a consequence of melt water activity but modified by more recent climatic and anthropological intervention. Much of the hilly area is now managed as heath and woodland.

The Bracklesham Group of sands, in common with many sand deposits, consist mainly of silica and silicate particles of size 0.05-0.15 mm (fine to medium sand). This was originally sorted and deposited in shallow marine, lacustrine or estuarine environments, and progressively buried under anaerobic or anoxic conditions. Adventitious secondary mineral phases include:

- finer and coarser silicates (e.g. clay and gravel mentioned above) and variable clay-rich lenses;
- hydrated iron(III) oxide ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$, often approximated as amorphous $\text{Fe}(\text{OH})_3$);
- partially crystalline ferrihydrite or fully crystallised goethite;
- calcite (CaCO_3);
- organic detritus (sometimes approximated as CH_2O); and
- reduced or partly reduced minerals, e.g., pyrite, siderite (or ironstone) and glauconite (nominally FeS_2 , FeCO_3 and $\text{KAl}_{3/4}\text{Fe}(\text{III})_{3/4}\text{Fe}(\text{II})_{1/4}\text{Si}_4\text{O}_{10}(\text{OH})_2$, respectively).

Concentrations of these minerals can be locally high, for example siderite in so-called iron pan within the Camberley Sand and glauconite (up to 75%) in the Windlesham Sand formations. Sulphide species with higher Fe:S ratio, e.g., pyrrhotite (nominally $\text{Fe}_{0.9}\text{S}$, although often written FeS) might also be formed, but are rare in ancient low temperature sedimentary environments (Goldhaber, 2005), presumably because of metastability with respect to pyrite.

Sand is typically permeable to groundwater, although quite small proportions of dispersed <20 µm particles or thin interbedded layers of silt and clay may variously hinder flow, create perched stagnant volumes and give rise to springs and seepages at different levels. In the present case, most groundwater apparently flows finally from the basal interface between the Bagshot Sand Formation and underlying clay (implying vertical continuity), but smaller outflows occur at higher elevations. For instance, observation of borehole samples and field exposures (MacMillan & Mather, 1998) indicate springs and seepages at or near interfaces between the three sand horizons, for example, between the Camberley and Windlesham sands (the latter being generally more clay rich but topped with a high conductivity pebble layer) and between the Windlesham and Bagshot sands (which are discontinuously separated by the so-called Swinley Clay Member). The different sands may in fact be defined, at least in part, by the dividing effects of volumes or layers of lower or higher permeability.

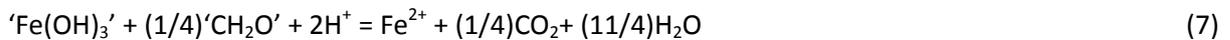
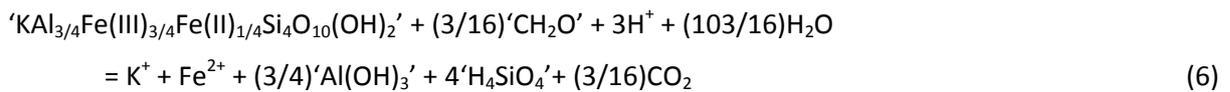
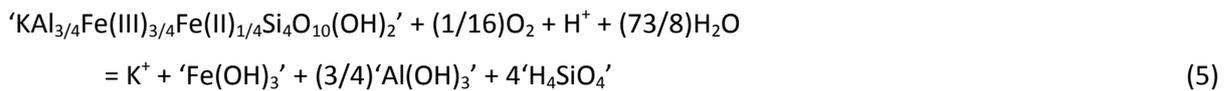
Rainwater percolating from the surface is normally near-saturated with oxygen from air (about 10 mg/L O₂) at near-ambient temperature, low in dissolved salts (conductivity <10 µS/cm) and slightly acidic (about pH 5.5 from dissolved carbon dioxide and possibly lower from acidic contamination, for example, by sulphur dioxide). Groundwater emerging, at whatever level, is normally low in oxygen (DO <1 mg/L O₂) at about 10°C, increased in dissolved salts (conductivity roughly 200-400 µS/cm) and variable in acidity (pH 3-6). Although chemical reactions, for example, oxidation/reduction and dissolution (or leaching) and precipitation, occurring at low concentration underground are uncertain, reference to standard texts (e.g., Stumm & Morgan, 1996) suggest that:

- oxygen is consumed at relatively high E_h (about 0.4-0.7 V) by microbially-mediated organic degradation and progressive mineral oxidation (particularly of sulphide and iron(II));
- conductivity increases from dissolution of more soluble and abundant minerals, e.g., gypsum (CaSO₄·2H₂O); and
- acidity arises from plant products, e.g., humic and fulvic acids, and/or hydrogen ion from sulphide oxidation.

Once oxygen is removed, weaker oxidants, particularly iron(III) in Fe(OH)₃, may participate in reactions catalysed by anaerobic bacteria at lower E_h (about 0 V) yielding mobile ferrous iron, which later emerges in groundwater at springs and seepages. Many reports of anaerobic iron(III) reduction in sediments have been published, for example, Lovley & Phillips (1986).

Reactions occurring underground are usefully approximated by thermodynamic equations, for example, Equations (1-8), despite true equilibrium being unlikely under the variable mineralogical and flow conditions prevailing in sand masses. This assertion can be made, even though standard free energy changes (not shown) may be unfavourable in particular cases for the forward processes represented and (being relevant primarily to thermodynamically closed or isolated systems) cannot directly predict that those processes might still occur significantly in (thermodynamically open) geochemical systems. In other words, notwithstanding theoretical shortcomings, and uncertainties in the precise nature and quantity of reactants/products (particularly where indicated by inverted commas in the equations) or in the detailed kinetics of the groundwater-solid interactions, reaction trends and proportions are still plausibly modelled by formal material and charge balances. Thus, such equations enable the general form of possible overall changes to be formulated and the comparative behaviour of individual species, for example, hydrogen ions, to become clearer.





For near surface regions where dissolved oxygen is present (relevant to the so-called oxidised zone), Equations (1-5) predict, in turn:

- oxidation of organic matter, ultimately to dissolved bicarbonate and carbon dioxide (the proportions depending upon pH);
- of siderite to insoluble hydrated iron(III) oxide and carbon dioxide;
- of pyrite to soluble iron(II) and sulphate;
- of iron(II) to hydrated iron(III) oxide; and,
- of glauconite to the insoluble products hydrated iron(III) oxide, 'aluminium hydroxide' and 'silicic acid', together with aqueous potassium ions.

In fact, glauconite is variously reported to leach incongruously leaving a residue of goethite, alumina, pyrophyllite and/or kaolinite depending upon prevailing conditions, but this variability does not materially affect the form of Equation (5) for present purposes. As a result of oxidative weathering, well-formed siderite, pyrite and glauconite become yellow-brown (from typically yellow, brassy and green, respectively) as they progressively convert to hydrated iron(III) oxide. Depending upon relative concentrations in different oxidising strata, these minerals may give rise to substantive iron accumulations, for example, in 'ironpan', as mentioned above, analogous to a reported horizon of 'red bed' hydrated iron(III) oxide (e.g., Parron & Nahon, 1980). Some iron(II) (Equations (3) and (4)) may flow to the reduced zone thus escaping oxidation. Equations (1) and (2) indicate broadly unchanged pH, although oxidation of acidic organic matter might lead to a slight increase in pH underground while dissolution of carbon dioxide might maintain pH in the range 5-6. Equations (3) and (4) predict significant reduction in pH, as has been observed in analogous reactions in so-called 'acid mine drainage' (Pipkin *et al.*, 2005). Equation (5), represents glauconite weathering, indicating a pH increase. Additionally, small concentrations of iron(III) may become mobile, primarily as colloidal sized particles or in complex species with humic substances (Tipping *et al.*, 2002).

In isolated, oxygen-free, volumes (in the so-called reduced zone), pyrite and glauconite may occur together in stable close association, even though glauconite contains about 75% iron(III) under these conditions (Fanning *et al.*, 1989). Siderite should also be stable. However, in the presence of groundwater flow, cation exchange in glauconite (especially hydrogen ion for potassium ion), followed by reduction of iron(III) (Equation (6)), or similarly in oxide (Equation (7)), by organic matter should be possible to form soluble iron(II). Such a reaction would probably occur through microbial catalysis at E_h about zero volt and would tend to increase pH. Percolating hydrogen ion (e.g., from pyrite oxidation in the oxidised zone, Equations (3) and (4)), may also in principle host acid-base reaction to yield similar mobile iron(II) if significant siderite mineralisation occurs (Equation (8)).

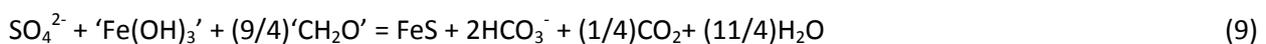
These reactions are evidently slow and partial under the geochemical conditions encountered yielding the low (0-20 mg/L) concentrations of dissolved species typically observed, year after year. Sparingly soluble but more abundant minerals sometimes leach more freely and rapidly to give relatively large concentrations of other ions (5-200 mg/L), especially calcium, sodium, magnesium, potassium, chloride, sulphate and bicarbonate (Carlisle & Dudeney, 2000a).

Groundwater normally emerges clear and colourless from the sands and is diluted in local streams either directly or, more commonly, indirectly via peaty wetland systems resting on an impervious base,

commonly clay. The water then becomes increasingly cloudy as contained iron(II) oxidises to hydrated iron(III) oxide, often termed ochre. The oxidation process is likely to be catalysed by biological and mineral surfaces on which iron(II) and oxygen adsorb (and can thus react more efficiently in close proximity), particularly by 'cushions' or 'mats' of 'iron bacteria', for example, *Leptothrix ochracea* and *Gallionella ferruginea*. Such bacteria are often abundant in wetlands containing iron(II), which promotes their growth (Ferris, 2005; Carlile & Dudeney, 2000b). Accumulated residues of resulting bacteriogenic iron oxides provide mineral/organic support for the growth of other wetland plant species such as mosses, grasses, sedges, rushes and alders. Thus, iron(II), bacteria and resulting ochre together cause the characteristic orange-brown festooned appearance of stream beds, banks and vegetation in contact with iron-rich water and, more generally, are probably responsible for the very existence of wetland features and peat deposits in the local environment.

Numerous ochreous wetlands (mostly <1 ha in area) occur in the vicinity of the Bracklesham Group with receiving streams becoming cloudy and margins becoming coated in ochre from oxidation of residual iron(II) escaping these areas, decreasing in intensity but remaining visible sometimes for as far as 1 km downstream. The wetlands were once probably larger, before drainage, peat cutting and community development (Hughes, 1890), and analogous to more extensive geological systems elsewhere linked to the formation of bog iron ore (Postgate, 2000). Nowadays ochre cannot significantly increase the size of wetlands through deposition because of community land use but is transported discontinuously in suspension downstream, together with organic detritus; mobilised by the action of rainfall or other disturbance. Being highly hydrous, largely amorphous, and low in density, ochre does not sediment readily and most finally discharges with river water to the sea. However, some ochre becomes physically trapped, at least temporarily, especially behind accidental obstructions or constructed dams (and associated ponds or lakes in which relatively low linear flow rates promote sedimentation).

The resulting soft clay-like sediment is orange in colour at the surface, but at >2-3 mm depth often becomes black owing to bacterial sulphate reduction. This occurs at the slightly alkaline pH 6-8 and low E_h -0.4 to -0.2 prevailing, yielding gelatinous black iron(II) sulphide (Equation (9)). This is normally the first-formed sulphide product, although it may later be oxidised to pyrite. The well known 'bad egg' odour of hydrogen sulphide is not normally detected because essentially all is trapped by iron at the pH in question. However, pore water at depth typically contains significant concentrations of iron(II), this species being in excess over sulphide. Dissolved iron(III) is also detected, probably complexed with humic substances. In deeper sediments bacterial methanogenesis may also occur at E_h about -0.4 V, resulting in methane and carbon dioxide evolution (Equation (10)). These sediments have increased pH (up to 8), probably as a result of both iron reduction and gaseous evolution. Precipitation of iron(II) carbonate should also occur at higher pH, essentially via the reverse of Equation (8), with hydrogen ions being neutralised by the prevailing alkalinity. The precipitation of iron in these ways may be contrasted with its possible modes of mobilisation in sand underground (Equations (3), (6)-(8)), reactions presumably occurring at lower pH and higher E_h unsuited to bacterial sulphate reduction.



From the foregoing, an overall picture emerges of low-lying, sandy heathland hills with geochemically or biogeochemically mobilised iron from pyrite, siderite, glauconite and/or hydrated iron(III) oxide in a reduced state in groundwater. This flows at various elevations to springs or seepages associated with small peaty wetlands on clay, the iron oxidising in air and precipitating as red-brown ochre, both in the wetlands and for some distance downstream. Occasionally disturbed ochre disperses discontinuously and flows with drainage towards the sea; but may be sedimented at obstructions, buried, re-reduced and re-immobilised as a soft black mixture rich in amorphous mineral phases similar to pyrrhotite and siderite. The picture at the surface is one of boggy areas in many locations associated with: orange, brown, and black sediment; opaque streams; and particular wetland organisms and vegetation extending along many kilometres of streams and small rivers.

REFERENCES

- CARLILE, M.J. & DUDENEY, A.W.L. 2000a. Iron transport and retention in ochre-rich water courses *Mineral Resources Engineering* **9**, 357-375.
- CARLILE, M.J. & DUDENEY, A.W.L. 2000b. A microbial mat composed of iron bacteria. *Microbiol.* **146**, 2092-2093.
- ELLISON, R.A. & WILLIAMSON, I.T. 1999. *Geology of the Windsor and Bracknell District – a Brief Explanation of the Geological Map Sheet 269 Windsor*. British Geological Survey, Keyworth, Nottingham.
- FANNING, D.S., RABENHORST, M.C., MAY, L. & WAGNER, D.P. 1989. Oxidation state of iron in glauconite from oxidised and reduced zones of soil geologic columns. *Clays and Clay Minerals*, **37**, 59-64.
- FERRIS, F.G. 2005. Biogeochemical properties of bacteriogenic iron oxides. *Geomicrobiol. J.* **22**, 79-85.
- GOLDHABER, M.B. 2005. Sulfur-rich sediments. In: MacKenzie, F.T. (ed.) *Sediments, Diagenesis and Sedimentary Rocks*. In: Holland, H.D. and Turekian, K.K., (executive eds.), *Treatise on Geochemistry* **7**, Elsevier, Amsterdam, 257-288.
- HUGHES, G.M. 1890. *A History of Windsor Forest, Sunninghill and the Great Park* Ballantine Hanson, London and Edinburgh.
- LOVELY, D.R. & PHILLIPS, E.J.P. 1986. Organic matter mineralisation with reduction of ferric iron in anaerobic sediments *Applied Environmental Microbiol.* **51**, 683-689.
- MACMILLAN, J.M. & MATHER, J.D. 1998. Groundwater quality variations in the Eocene Bagshot formation UK. In: Arehart and Hulston (eds.) *Proc 9th International Symposium Water-Rock Interaction*, Balkema, Rotterdam, 161-164. ISBN 9054109424.
- PARRON, C. & NAHON, D. 1980. Red bed genesis by lateritic weathering of glauconite sediments. *J. Geol. Soc.* **137**, 689-693.
- PIPKIN, B.W., TRENT, D.D. & HAZLETT, R. 2005. *Geology and the Environment 4th Ed.* Brooks/Cole Thomson Learning Inc., Belmont, USA.
- POSTGATE, J.R. 2000. *Microbes and Man, 4th Ed.* Cambridge University Press, Cambridge.
- STUMM, W. & MORGAN, J.J. 1996. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters, 3rd Ed.* John Wiley and Sons Inc., New York.
- TIPPING, E., REY-CASTRO, C., BRYAN, S. & HAMILTON-TAYLOR, J. 2002. Al(III) and Fe(III) binding by humic substances in freshwaters, and implications for trace metal speciation. *Geochem. et Cosmochim. Acta.* **66**, 3211-3224.