Spatial and temporal relationships between Eocene sand horizons and iron contamination in stream water in the Thames Basin west of London, UK

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ABSTRACT: Analyses of stream water samples associated with Tertiary (Eocene) sands of the Bracklesham Formation 30-60 km west of London showed numerous occurrences of groundwater containing elevated iron(II) concentrations (1-15 mg/l Fe), which oxidise to red-brown ferrihydrite in localised wetlands and streams and join onward flows towards the River Thames. GIS mapping of iron concentrations in relation to topographical and geological data within a 20x30 km project area indicated some 168 km of iron-contaminated water.

The results are consistent with downward permeation of groundwater through contained Camberley, Windlesham and Bagshot sand horizons and predominant W-E groundwater flow of up to 35 km in the Bagshot horizon, which rests on impermeable London Clay. Glauconite, comprising up to 70% of the sand near the base of the Windlesham horizon, apparently provides the main source of soluble iron in the near-

26 anoxic, near-neutral, conditions normally prevailing. Pyrite is also a possible source,
27 especially where quarrying or other excavation releases water from previously
28 isolated volumes, simultaneously causing elevated sulphate and acidity levels via
29 relatively rapid sulphide oxidation. Mechanisms proposed are underpinned through
30 comparison with reports on analogous systems in the UK and abroad.

31 Streams and lakes in the vicinity of seepages are highly visible and of
32 decreased biodiversity. However, because of their natural origin, they are not subject
33 to the same public concern and environmental control as compositionally similar
34 near-neutral water from many former coal mines elsewhere - where iron derives
35 primarily from pyrite. Also, while comparatively persistent, they appear destined for
36 rapid depletion in geological terms: the unusual isolation of the sands until the
37 Quaternary indicates a short leaching period and suggests a reason why iron-rich
38 water from natural ferruginous sands is seldom of sufficient significance to be
39 reported.

40
41 **KEYWORDS:** *Eocene sand, groundwater flow, iron mobilisation, stream water*
42 *mapping, environmental impact*

44 INTRODUCTION

45
46 Sedimentary deposits commonly contain iron minerals which may leach to drainage
47 water when exposed through geological change or anthropological excavation. When
48 such leaching occurs, receiving rivers and immediate surroundings may become
49 orange-brown in appearance from processes considered, depending upon their origin,
50 to be 'natural' (occasionally giving rise to sites of special scientific interest) or 'man-

made' (potentially causing pollution and unwanted reduction in biodiversity). In the UK, for instance, the California Country Park (CCP) in Berkshire, UK (Wokingham Borough Council 2012), features 'rare ancient bogland and lowland heath', and has a public walkway across a 'natural' Fe-rich discharge and wetland located in between a source of iron in local sand deposits and tributaries of the River Thames. By contrast, the Bullhouse Minewater System in Yorkshire, one of many treatment systems maintained by the UK Coal Authority (Coal Authority 2012), mitigates the analogous 'man-made' effects of Fe-rich water from abandoned sedimentary coal measures ahead of discharge, in the case mentioned to the Upper River Don (Dudeney *et al.* 2000).

Iron-rich drainage from industrially-worked ground, particularly from worked coal measures and sedimentary (or other) base metal deposits containing pyrite, has received much attention internationally, because of potentially deleterious environmental effects in receiving rivers - unsightly visual impact, particulates smothering benthic organisms and/or dissolved pollution (iron, acidity, toxic metals and/or anions) - and, conversely, because of value as a source of water. Many studies have reported the characteristics and management of such Fe-rich drainage, which may typically be at pH <4 as a result of acid generation from pyrite leaching or pH 5-7 when buffered through concomitant contact with carbonate or other acid-consuming strata. Following research and development over decades, going back before the turn of the 20th Century (e.g. Swallow 1891) and including various well-reported academic reviews (e.g. Blodau, 2006) and books (e.g. Lottermoser 2010), most relevant characteristics of these contaminating discharges are now understood. However, practical mitigation of the discharges (of which thousands exist worldwide) continues to represent one of the most difficult legal and economic problems facing the

international mining industry. In particular in Europe, cleaning rivers of this mining effluent is costly in terms of land, plant and operation, without generating significant revenue, but is required to meet the provisions of the Water Framework Directive (European Commission 2000) - relevant to 27 countries - that all rivers should be of good ecological status by 2015.

By contrast, natural analogues at similarly low temperatures have received little attention (Blodau 2006). They may often be observed in the environment but apparently usually amount to no more than small, insignificant, seepages. However, the discharge at CCP is one of a number of substantial Fe-rich springs, linked to erosion and leaching of porous sandy deposits in South-East England, particularly those exposed on high ground to the west and southwest of London (Fig. 1), i.e. draining to the London Basin (Rae & Parker 1992) and Hampshire Basin (Curry *et al.* 1977). Thus, the effects of substantial iron-rich groundwater are observed in many local streams and wetlands in the counties of Berkshire, Surrey and Hampshire.

The sands of these counties, termed the Bracklesham Group - largely of Tertiary age (Eocene 44-50 Ma) and generally considered to be of lacustrine origin - have received considerable attention from geologists (e.g. Ellison & Williamson 1999; Mathers & Smith 2000; Ellison *et al.* 2002), but the Fe-rich water emerging from them, notwithstanding its highly visible impact, is emphasised in relatively few cases (e.g. MacMillan & Mather 1998). An exception is the so-called 'Red Stream of Swinley' (Hughes 1890) or 'Red Stream', which flows *c.* 3 km from South Ascot, formerly 'The Bog', (Hathaway 1995) to a man-made Fe-rich lake and wetland, originally a fish pond for landed gentry, at the Silwood Park Field Station of Imperial College (Carlile & Dudeney 2000; Crawley 2005), and then, with less visible coloration, on towards the larger public attraction of Virginia Water Lake. Staff and

101 students of the College have produced numerous scientific reports, mostly
102 unpublished, about this interesting but somewhat hazardous boggy South Ascot-
103 Silwood Park system. With the advent of high quality GPS and GIS, more recent
104 reports have included many similar systems in the surrounding area (the project area)
105 covering some 20x30 km (Fig 1). Recent contributions have also been made by staff
106 linked to Wokingham Borough Council, which has responsibility for NW parts of the
107 area, including CCP. To satisfactorily represent the large quantity of raw data
108 accumulated, particularly Fe concentrations, a GIS-based map, represented digitally at
109 1:50000 (A0) scale, has been made available on the BGS (British Geological Survey)
110 website, together with background descriptions and underpinning theoretical
111 considerations (Mason *et al.* 2010). This work is thus linked to the BGS GBase
112 surveys of England and Wales (Johnson *et al.* 2005).

113 The present paper rationalises information obtained in the project area,
114 including data from essentially all substantive Fe-rich discharges draining towards the
115 River Thames. It is intended to provide a clearer understanding of the modes of
116 occurrence and gravitation of Fe-rich groundwater in relation to its geological and
117 mineralogical setting, particularly involvement of glauconite and pyrite, and patterns
118 of flow. The possible impact of siderite and other Fe-containing phases are also
119 mentioned. Complementary aspects of surface observations and previously published
120 borehole data are highlighted. More generally, the work is set in the context of
121 available reports of geochemical changes in analogous sand deposits in the UK and
122 abroad. The paper also compares observed characteristics and environmental impacts
123 with those of analogous discharges of ‘man-made’ and ‘natural’ origin, including
124 further unpublished observations from Imperial College students.

The paper thus has three main objectives: reporting (particularly through GIS representation) the spatial distribution and intensity of elevated Fe and other concentrations in the project area (surface distributions), comparative interpretation of hydrological and geochemical processes involved in Fe release from the sedimentary deposits (underground mechanisms), and assessment of significance in the surface environment and longevity (surface impacts).

METHOD

Fieldwork, sampling and testing

Fieldwork was carried out over a 15-year period, but mainly by students engaged on risk-assessed project assignments during the period 2005-2008. The method employed was primarily that of Carlile & Dudeney (2000), augmented by GPS positioning in relation to maps of the project area (Fig. 1): 1:25000 OS Explorer Maps No 144, 145, 159 and 160 (Ordnance Survey, 2004, 2005a, 2006 and 2005b, respectively) and 1:50000 BGS Solid and Drift Maps No 268, 269, 284 and 285 (British Geological Survey 2000, 1999, 1980 and 2001, respectively). Work presented here was based mainly on analyses of ground and stream water, but not solid samples (because of likely contamination of material recovered at the surface). Identification of strata was thus made largely from the geological sheets cited and qualitative interpretation. Routine observation (weather and surroundings) and sampling were carried out in the vicinity of any accessible and undisturbed Fe-rich springs, seepages and streams known from previous work or discovered during fieldwork. Note was taken of any risk from anthropological contamination, e.g. by discharge from local properties. Observations were recorded according to a standard

booking procedure employed for many years in the Department of Earth Science and Engineering at Imperial College London. Permission was sought to sample on private ground. Local people and organisations were approached for impressions of the impacts of Fe-rich water.

Water was analysed directly by electronic probe for pH (WTW pH 325i), dissolved oxygen (WTW Oxi 320), conductivity (WTW Cond 330i) and temperature, and indirectly for Fe and sulphate (Hach DR2010 portable spectrophotometer) and 27 other ions (ICP emission spectrometry, Natural History Museum, London). Where appropriate, measurements were temperature-compensated. Iron(II) was stabilised on site (typically in 30-ml graduated 'Steralin' tubes) by means of powder 'pillows' (sachets containing set small quantities of necessary reagents) as the red iron(II) *o*-phenanthroline complex for later DR2010 measurement. Total iron was similarly measured after subsequent addition of FerroVer 'pillows', which contained a reducing agent. Small concentrations of suspended particles had insignificant effect on iron(II) determined by this method, although filtration via a 0.2- μ m membrane filter was occasionally necessary. The precision of water sampling and analytical measurement were typically 2-5% relative.

Spatial modelling

A digital database was constructed, using ESRI's ArcGIS, to hold all sample records, stream vectors, maps and analytical data. ArcGIS was then used for manipulation of digital map and analytical data and for visualisation and presentation in digital map form covering the whole project area, nominally at the 1:50000 scale.

The base geological map was constructed by merging digitised data (provided by BGS under licence) from appropriate parts of BGS 1: 50000 solid and drift sheets

for Basingstoke, Windsor, Reading and Guildford (BGS 1977, 1999, 2000, 2001, respectively). Topographic mapping was provided by OS 1:10,000 scale digital topographic map, OS Panorama and Profile Digital Terrain Models (DTMs, at 50-m and 10-m grid size, respectively), and augmented by digital aerial photography (all provided under OS academic licensing agreements). Stream vectors were calculated from an OS Panorama Digital Terrain Model (50-m grid size). A stream vector dataset was generated using the Panorama DTM, and the individual stream segments simplified and smoothed for the purposes of presentation. Comparison with 1:10,000 scale OS topographic maps and digital aerial photography was employed for correction of, and addition to, the stream channel dataset.

The analytical results from stream samples were binned (e.g. into several ranges of concentration) in order to provide a simplified code which could be linked with the stream vector data, thus allowing data such as increasing Fe concentration to be visualised per stream segment. The coded analytical values were then joined to the relevant drainage channel segment enabling the stream segments to be symbolised accordingly; in maps presented here each stream segment is colour-coded from blue to red, to represent a total of seven levels (bins) of increasing total Fe concentration. The solid and drift geology polygons were simplified and overlain on the OS 1:10000 scale digital topographic map, along with surface water courses, numbered sample locations, watersheds and the coded stream segments to produce the final map. Figure 2 exemplifies the stream segments, which had been constructed such that Fe concentrations along the stream changed only when a sample point of a different value was encountered, and only downstream of that sample location.

Two geological cross-sections were produced based on cited geological maps, highlighting the sequences of strata and rise/fall of elevation. Two further cross-

sections, following selected watercourses, emphasised Fe concentrations in streams in relation to underlying geology. In this case Profile DTM was used to extract topographic profiles along the line of the watercourse and geological cross-sections were drawn beneath these profiles. Linearly referenced stream channels were plotted alongside them to enable examination of the relationship between lithology, topography, hydrology and the occurrence of iron contamination at the surface.

RESULTS AND DISCUSSION

Surface distributions

The complete map is too large to be fully represented here but may be viewed, with all sample sites uniquely identified by number, at the BGS website (Mason *et al.* 2010). Figure 3 shows a scaled-down and simplified version, covering the entire project area. A vertical merging mismatch evidently occurs between the Guildford and Basingstoke sheets at SU 4815 1590, probably because the Basingstoke sheet was not updated (as were the other sheets employed) after 1977. The map highlights the main areas of the Bracklesham Formation (Camberley, Windlesham and Bagshot Formations) forming low hills up to 120 m in elevation above local deposits of underlying London Clay. Small areas of the same sand formations occur immediately to the east and west of the map boundaries. The map includes drift geology but, for clarity, omits Quaternary river terrace deposits. Towns and other locations (where relevant to the discussion) are shown as dots even though they actually cover substantial areas of the map.

Associated geological memoirs (Ellison & Williamson 1999; Mathers & Smith 2000; Ellison *et al.* 2002) describe the main surface characteristics and

225 sequences of horizons with depth. The highest land is in the south of the project area
226 (188 m AOD) to the west of Aldershot and the lowest in the northeast (20-30 m AOD,
227 near Virginia Water town); notwithstanding intervening hilly areas and several
228 watersheds, strata dip generally towards the east (as is commonly the case in the
229 London Basin). The whole area is drained to the Thames (NE corner of the map) by
230 the Whitewater and Blackwater (tributaries of the Loddon, to the W and N), the
231 Bourne (N and S arms, to the E and NE) and the Wey (to the SE). The Wey cuts
232 through the chalk of the North Downs (<150 m AOD), which follow a line E-W
233 immediately south of the project area (not shown on Fig. 3).

234 Stratigraphic cross-sections are inferred from borehole logs and contours. In
235 particular, the relatively recent Mytchett No 1 and No 2 boreholes in the Blackwater
236 Valley (SU 8833 5541) prove some 35 m Camberley Sand, 17 m Windlesham Sand, 4
237 m Swinley Clay (maximum 8 m), and (the upper) 3 m Bagshot Sand at that location
238 (Ellison *et al.* 2002). Outcrops of all formations occur but exposures are mostly
239 obscured by Quaternary deposits and anthropological cover. Two representative cross
240 sections, identified by straight lines running E-W and SW-NE in Figure 3, are shown
241 in Figure 4. One of these lines runs close to the location of the Mytchett boreholes.
242 Figure 4 highlights the continuous, undivided, nature of the Bagshot and London Clay
243 Formations and the ways in which the Windlesham and Camberley Formations rest in
244 sequence above them. Other boreholes consider the deeper formations shown,
245 particularly Lambeth Clay Beds and Thanet Sands (Paleogene) and Chalk, Gault Clay
246 and Folkstone Sand (Upper Cretaceous).

247 Iron-rich groundwater was usually observed as a cloudy orange flow joining
248 steams (directly or via wetland areas on their banks) just below their emergence as
249 springs or, as less-well defined seepages, along varying lengths of stream courses

downstream. Based on on-site electronic probe analyses in the present work, such emergent groundwater, sampled at locations largely free from surface contamination, was at or near temperature 10 °C, pH 6-7, DO 10-20% of full saturation and λ 0.2-0.4 mS/cm, data which probably quite closely reflected most conditions underground. Groundwater was most readily distinguished in the field from general drainage by its low DO. In analogous borehole studies, Macmillan & Mather (1998) noted that pH increased from 4.0 to 6.5 with depth in the Bracklesham Formation.

However, in that study and the one reported here, samples taken at surface were usually affected by variable dilution in surface water, contact with boggy ground or air during sampling, and changes in ambient conditions. Surface water samples were also subject to contamination from anthropogenic practices such as fertiliser use. Most data recorded were therefore of qualitative or semi-quantitative significance. However, although Fe contents varied substantially both spatially and temporally within the project area, there was no apparent overriding change in the general character of the water through most of the project area, which, except perhaps at points of groundwater seepage, could thus usually be considered as stream drainage containing variable concentrations of Fe.

Some 440 surface water sampling points are shown (as small open circles) in Figure 3. Sites specifically discussed are further indicated by red squares (designated 'heavily contaminated sites'). The sampling points mainly relate to sites on Bagshot and Windlesham Sand and surrounding margins of London Clay. Only small numbers are shown for Camberley Sand because of fewer streams and restricted access in some areas (mainly built over or used by the military) at the surface. Approximately half of the sites, predominantly on sand, have elevated Fe concentration (1-15 mg/l Fe(II)) and visible Fe(III) deposits. However, individual Fe

275 concentrations are not shown (although sites are uniquely numbered and linked to
276 separate numeral data on the BGS website version). Estimated lengths of streams in
277 the vicinity of points containing elevated Fe are represented (in decreasing order of
278 concentration) by shades of red, orange and yellow. Lengths of Fe-contaminated
279 water can thus be seen associated with the three sand types but estimated to be
280 decreasing in Fe content in the order Bagshot>Windlesham>Camberley Sand. Visible
281 Fe usually decreased to zero <1 km downstream from seepages but resulting, less
282 visible, solids are expected to be carried in suspension towards intervening lakes and
283 the sea, especially during heavy weather. The total stream length of Fe-contaminated
284 water was calculated in ArcGIS, as the sum of Euclidian distances between each
285 vertex of the 1003 stream/river segments, to be 168 km, the average segment length
286 being just less than 1 km.

287 Notwithstanding effects of dilution, oxidation and sundry contamination, and
288 in line with hydrological supposition (see below), elevated Fe concentrations clearly
289 predominate in stream valleys associated with (the base of) the Bagshot Sand in the
290 east and northeast of the project area (Figs. 3, 4), especially where closely underlain
291 by less permeable clay horizons. In particular, most of the length of the Red Stream
292 running E-W from South Ascot to Silwood Park (3 km) receives Fe-rich seepage as
293 does a roughly parallel stream (on the south side of the Silwood watershed) running
294 from Old Windsor Bog near Sunningdale train station to the (man-made) Virginia
295 Water Lake. The lake itself is apparently deep enough to preclude Fe-rich seepage
296 along its 3-km length but below the 4-m vertical exit cascade to the River Bourne (N
297 arm), flowing southeast, seepage immediately reappears and, together with Fe-rich
298 water from several more streams, continues c. 3 km through the Wentworth Golf
299 Course and Cabrera Trust Land to Virginia Water Town, after which visible Fe

decreases rapidly to below detection as the river flows away from the sand. Cabrera Trust Land was additionally observed to receive numerous seepages via short side-streams on wetlands flanking the Bourne. Over this stretch, the river runs at the interface between the Bagshot Formation and the underlying Claygate Member (Fig. 4). During periods of low flow, direct seepage beneath the water surface could be seen as orange cloudiness emerging from both banks of the River.

The underlying geology, in relation to Fe content in the surface streams, is exemplified in the cross-section in Figure 5, following the full course of the valley, shown as two drainage channels flowing approximately perpendicular to the regional bed dip: one flowing into and the second flowing out of Virginia Water. Once again the highest concentrations of Fe are (finally) associated with the Bagshot Sand, although in this image much Fe-rich water clearly originates from the Windlesham horizon, flowing along a stretch of low permeability Swinley Clay, towards lower ground.

The River Bourne (S arm) collects smaller, but still highly visible, quantities of Fe via seepages from the south and southeast flanks of the sand, mainly via the Windle Brook, Stanford Brook and Hoe stream. Substantial Fe concentrations were also observed in the northwest of the region, in particular around and immediately to the east of the aforementioned CCP, and to the south near the Cemex Quarry, all presumably arising from a subsidiary dip in strata exiting at surface in those directions.

Thus, although streams in the project area appear, at least near their source, to emanate towards all points from the sand masses (Fig. 3), seepage and drainage to the east as a whole apparently account for most of the Fe contamination, consistent with the effective trend of dip of the strata. It should be noted that the Bagshot Formation

is largely below river level (13-16 m AOD) near the east end of Section 1 (Figs. 3, 4), with Quaternary cover (not shown) at ground level.

Figure 6 gives two scatter plots showing pH and sulphate concentration versus Fe(II). Most results are seen to cluster in the ranges pH 6-8, sulphate 20-110 mg/l and Fe(II) 1-3 mg/l, without clear correlation. A similar lack of correlation can be seen with other cations, including K. However, general similarities in most results underpin the notion of similar origin, while several outliers give insight into differences. Thus, water samples taken at the Cemex quarry workings, which extracted Quaternary fluvial sand and gravel until recently from the River Blackwater flood plain near Eversley, indicated (summer 2007) low pH (3.0), high sulphate (250 mg/l) and moderate Fe(II) (6.0 mg/l). The samples were taken at the sand/clay interface between the Bagshot Formation and London Clay where quarrying had shortly before exposed new vertical surface. The results, which were not significantly affected by quarry residues, suggested release of previously isolated (reduced) volumes of groundwater having different geochemistry. Such low pH could possibly arise from humic acid in peaty drainage or from oxidation/hydrolysis of relatively large concentrations of Fe(II), but was likely to be primarily associated with oxidation of sulphide in pyrite. Patterns of orange Fe(III) oxide precipitates on the newly exposed quarry face suggested channelled flow, apparently analogous to that observed by Barral & Guitian (1991). This notion is re-visited in the next section.

Table 1 shows analyses at five locations, three of which feature relatively low pH, all relevant to a particular sampling date. The samples contained (as more generally typical) substantial concentrations of Ca, Na, Mg and K, normally decreasing in that order, together with Fe. However, neither S (mainly as sulphate) nor **potash** could be linked closely with Fe by means of theoretical mole ratios,

Comment [G.F.1]: K?

consistent with remarks above. Various sources of the different ions evidently precluded such linkage. This substantiates the idea that the dissolved and suspended concentrations of surface streams, other than Fe content, are largely the result of surface interactions with rainwater and local discharges. Even in the case of ferrous Fe, a proportion (probably small except in the locality of recent excavations) is likely to originate in Quaternary and anthropological cover.

However, in the case of potash, an increase of some 20% in concentration in samples taken from a receiving stream (on Cabrera Trust Land) immediately upstream and downstream of an Fe-rich groundwater inflow indicated probable Fe release from glauconite (see below). A spring from Camberley sand had the lowest pH and lowest ion concentrations, expected from its location near the highest elevation of the system.

Underground mechanisms

It is supposed that the sands of the Bracklesham Formation are interconnected vertically and horizontally with respect to water movement under gravity, partially governed by elevations of outlets at surface. Thus, notwithstanding probable isolated volumes and layers of relatively impervious slit/clay and higher conductivity pebbles, the cross-sections indicated in Figures 3 and 4 (and others along complementary lines, not shown) predict a predominant flow from west to east (as indicated above), mostly within the Bagshot formation above stagnant volumes resting on the London Clay (especially beneath the Blackwater Valley). Overall flows and flow rates cannot be reliably estimated but are expected to be much lower than in typically well sorted sand because of low permeability (although high porosity) caused by relatively small sand particle size range, and often, contained silt and/or clay. The flows occurring are expected to carry initially oxygenated, and perhaps mildly acidic, water through the

375 system (maximum distance *c.* 35 km), progressively interacting with susceptible
376 minerals while leaving those in stagnant volumes largely unchanged. Within limits
377 (presumably) set by rainfall and seasonal water-table variation, and ground erosion,
378 this division of water character may have remained essentially unchanged through
379 millennia.

380 Iron minerals often observed in sand horizons include glauconite, pyrite and
381 siderite, all of which contain Fe in the divalent state, albeit in low proportion in
382 glauconite. Oxides (e.g. goethite) and Fe substitution in silts and clays (e.g. to give
383 Fe-rich smectite) also occur. For the Bracklesham Formation, the memoirs cited
384 indicate glauconite comprising up to 70% of Windlesham Sand near its base and the
385 same mineral scattered at lower abundance in Camberley and Bagshot Sand. Scant
386 mention is made of other Fe minerals although carstone (iron oxide cemented sand)
387 and iron stone (concretions of siderite) are reported to have been worked at specific
388 locations in the past.

389 As the present study has no direct access to minerals underground, related
390 studies provide complementary information, particularly regarding glauconite, pyrite
391 and siderite, which may be used to substantiate proposed Fe mobilisation
392 mechanisms.

393 Thus, Rae & Parker (1992) discuss phase associations of Fe, Mn and S in the
394 analogous Tertiary (Paleocene) Thanet Sands, which, together with underlying
395 Cretaceous Chalk, form the main aquifer beneath the London Clay and Lambeth
396 Beds. Fine-sized (framboidal) pyrite and sand-sized glauconite are implicated in Fe
397 contamination of water recovered during recharge, which is linked to ground water
398 flow in chalk from the Chiltern Hills *c.* 40 km to the north. Total Fe content in the
399 sand is substantial, varying in the range 1-6% total Fe. Loveland & Findlay (2006)

400 consider the disintegration of glauconite in Cretaceous Upper Greensand
401 (immediately beneath the chalk) in Southern England. Weathering processes to form
402 soils are considered to involve disaggregation of glauconite, translocation of clay,
403 removal of Fe(II) due to charge imbalance after loss of structural potash, and
404 oxidation of Fe(II) to form hydrous Fe(III) oxides. Illite-smectite also forms. Wolff
405 (1967) reports that weathering of Eocene sands in Maryland USA leads to goethite
406 pseudomorphs after glauconite, accompanied by re-precipitation in the form of a
407 white kaolinite coating, probably together with a mixed layer assemblage. Fanning &
408 Rabenhorst (1989) discuss differences in glauconite characteristics, particularly in the
409 oxidation state of Fe, recovered from so-called reduced and oxidised zones in 'soil
410 geologic columns' (silt loams and sandy loams) of Paleocene age in Maryland and
411 New Jersey, sampled to depths of 7 m. They observed that the Fe(II)/Fe(III) ratio
412 varied from 0.35 in the reduced zone (where the mineral was green in colour) to 0.0-
413 0.2 in the oxidised zone (where it was yellow). Fine-sized pyrite was always present
414 in the reduced zone, usually in intimate association with glauconite (sand-sized
415 pellets). However, it was absent in the oxidised zone (which contained Fe(III) oxides
416 and jarosite).

417 Barral & Guitian (1991) studied the formation of ferruginous accumulations in
418 Tertiary sandy sediments of NW Spain. Hard laminar crusts of goethite cemented
419 sand (cf carstone) are considered to have resulted from diffusion of Fe(II) to the
420 capillary fringe of a former water table or by oxidation and precipitation of Fe oxides
421 at the interface between sediment layers with different textures and different aeration
422 conditions. Globular and tubular accumulations are also discussed, the former
423 consisting of an indurated coat of goethite surrounding blackish, acidic, reduced
424 material containing Fe sulphides and sulphates, originally from the decomposition of

425 organic matter in a lacustrine environment. Tubular goethite precipitates are attributed
426 to the redistribution of Fe as the combined result of channelled water flow ('piping')
427 and diffusion of dissolved Fe(II) towards the unsaturated zone where it would have
428 been oxidized and precipitated. Globular and tubular deposits may be peculiar to the
429 deposits studied but nonetheless emphasise the probable roles of organics, differing
430 redox conditions and channels in Fe mineralogy and water flow in Tertiary sands.

431 The low temperature oxidation kinetics of pyrite are complex (Bierens 1990),
432 without directly suitable data available for present purposes, but the sulphide
433 component of fine-sized, uncoated pyrite is expected to oxidise relatively rapidly in
434 contact with partially-aerated water, releasing Fe(II) and sulphate. Siderite
435 degradation is also complex (McMillan & Schwertmann 1998; Tang & Martin 2011),
436 the mineral being subject to both oxidation and acid-base leaching. However, under
437 aerated conditions, both reactions produce goethite-like solids.

438 Taking account of foregoing information, reactive pyrite within, or near, zones
439 of steady flow in the Bracklesham Formation should already have progressively
440 oxidised, as occurs in abandoned coal measures. Pyrite in isolated (primordially
441 reduced) volumes should remain in place. However, if exposed to oxidation of
442 sulphide (but not Fe) it is expected to produce $\text{H}^+:\text{SO}_4^{2-}:\text{Fe}^{2+}$ in the mole ratio 2:2:1
443 and lead to reduction in pH to 3-4, other factors being equal. Partial oxidation of
444 Fe(II) is also likely underground, with further production of acid. Siderite (or its
445 degradation products) in the Bracklesham Formation should be relatively stable,
446 especially in massive form. Anoxic conditions with low enough pH (c. 3-4) could
447 lead to release of Fe(II) but are unlikely to be widely significant in these Tertiary
448 sands. Thus, although fully applicable data are not available, the main process
449 producing Fe-rich groundwater now is suggested to be non-oxidative release of Fe(II)

and K ion from glauconite in the Windlesham Formation component (fine to medium grained, clayey, sand), where a large concentration of this mineral has been stated to occur, consequent on destabilisation through ion exchange loss of K in near neutral medium (theoretical mole ratio $K^+ : Fe^{2+}$ of 1:0.25), with the main bulk of Fe(III) remaining in place (finally) as goethite. Other layer silicates subject to ion exchange loss may contribute, but are of much lower abundance. Microbial reduction of Fe(III) might also contribute Fe(II) concentrations and transport of Fe(III) without reduction, in the form of colloidal hydrous oxides or metal-organic complexes (to be reduced in receiving bogs), represents another possibility, but their significance cannot presently be substantiated. Notwithstanding these conclusions, further work is needed, employing fresh borehole solid and water samples, before the suggested predominant role of glauconite at the main source of mobile Fe can be fully accepted.

Surface impacts

Figure 7 shows a second set of analyses relevant to a particular date, in this case for seven types of locations on the Red Stream from South Ascot to Virginia Water Lake. pH is seen to increase marginally but reproducibly downstream in an increasingly bicarbonate buffered environment, from bog to fen to lake. The bog is a remnant of a much larger and more hazardous area which existed prior to drainage and development during the last century. Water seeping from it, as distinct from groundwater and stream water, is typically at pH 3-4. The fen environment in Silwood Park arises from a dam constructed across the Red Stream c. 200 years ago to create a fish pond. Inflow of dissolved Fe(II) and dispersed Fe(III) occur all along the course of the stream reaching maxima where seepage is greatest (on Bagshot Sand) immediately downstream of Sunninghill Bog. They decrease as dissolved and

475 adsorbed Fe(II) oxidises, and the resulting solid (ferrihydrite, as identified by XRD) is
476 carried away in suspension or (at low stream flow) settles to the bottom.

477 Concentrations of sulphate and nitrate are seen to increase variably
478 downstream, although nitrate levels are typically lower than on the date in question.
479 Others show no clear trend. Components and variations analogous to those in Figure
480 7 have been observed at CCP and other sites within the project area. All except Fe
481 concentrations originate mainly in surface water, the concentrations in which do not
482 correlate closely with the type of surrounding environment encountered.

483 However, the Fe deposits have a large impact on the immediate environment.
484 The Silwood Wetland (c. 2 ha) is mainly composed of vegetated Fe-rich sludge,
485 slowly encroaching into the Silwood Lake (1 ha), which is itself largely filled with the
486 same, but unvegetated, soft sludge held behind a 2-m exit cascade. Both wetland and
487 lake are preserved on College land as unspoilt wildlife habitats, but, in amenity terms,
488 they also represent hazardous environments because of the sludge (Mason *et al.*
489 2010). Nonetheless, despite visible impacts and potential hazards and changed
490 biodiversity throughout the project area, almost no adverse comment regarding
491 unsightliness, contamination or physical hazard has been received during surveys of
492 local comment over a period of 10-15 years. The local Environment Agency stated
493 that the Fe-rich environment is of natural origin and not of regulatory concern.

494 By comparison, analogous water of industrial origin, particularly ‘ochreous’
495 minewater, is strictly regulated, being ‘unnatural’, unsightly and detrimental to
496 wildlife and amenities (e.g. to trout fisheries: discharges at Fe(T) >2-5 mg/l typically
497 require clarification prior to discharge; Coal Authority 2012). For the purpose of
498 comparison, Table 2 shows representative ion equivalent balances for the Red Stream
499 and minewater at the former Bullhouse Coal Mine. As can be seen the main dissolved

500 species are the same, but, except for **potash**, have considerably greater concentration
501 in the minewater. In this, and other minewaters, the Fe content is linked to reactive
502 pyrite. Glauconite, having a different marine origin, is not expected in coal measures.
503 Owing to the high Fe(II) concentration in Bullhouse minewater, which produces more
504 acid upon oxidation and hydrolysis than can be neutralised by contained bicarbonate,
505 the minewater is 'net acid', changing in pH from 5.5 (fresh from underground) to 3.0
506 (at equilibrium, after several hours in contact with air). Examples of such
507 environmentally damaging 'acid mine drainage' occur worldwide at coal and metal
508 mines. Some also carry polluting concentrations of arsenic and/or toxic metals, which
509 may be co-precipitated with ochre. However, many coal minewater discharges have
510 lower Fe(II), contain insignificant other pollutants, are 'net alkaline' and, like their
511 natural analogues, have little impact other than high visibility on receiving water
512 courses.

513 Anecdotal evidence suggests that high Fe concentrations have persisted at
514 Bullhouse for more than 90 years since mine closure. However, in other cases
515 concentrations have decreased markedly after a few years 'flushing' of reactive pyrite
516 from underground workings and residual deposits. No doubt all deplete given
517 sufficient time. By comparison, observation of the Red Stream since the mid 1980s
518 indicates erratic changes in Fe content from year to year but no definite trend. Of
519 course, such a time-scale is likely much too short to observe a clear reduction of Fe
520 content in a geological system.

521 Conversely, rapid depletion *in geological terms* of reactive Fe (once exposed)
522 could account for rare occurrence, at any particular period, of substantial Fe-rich
523 discharges from natural sand deposits. Many sand deposits are ferruginous but
524 apparently produce insignificant Fe-rich water at the surface (e.g. the large older sand

deposits outcropping a short distance south of the present project area; Ellison *et al.* 2002). For instance, little visible Fe is seen in gravity drainage from the Folkstone or Hythe Formations, even though significant Fe mineralisation is recorded, together with ferruginous water at depth in specific wells. Effective Fe oxidation and gravity leaching to surface is perhaps largely complete. In contrast, the Bracklesham Formation has in all probability been subject to effective erosion and groundwater flow to surface only since the last ice age. There seems little doubt that the formation was relatively isolated prior to that time, unlike closely related (but now completely denuded) Tertiary cover, previously over the Folkstone, Hythe and associated formations (Thurrell *et al.* 1968). In this case, depletion of reactive Fe occurring now seems rapid. Thus, it is likely that the multitude of red streams available for study in the present project area has been made possible by very particular exposure of 50 Ma old sand deposits within just the last 0.1 Ma.

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 641 Wolff, R.G., 1967. X-ray and chemical study of weathering glauconite. The
 642 American Mineralogist 52, 1129-1138.
 643
 644 Table 1. Examples of pH values and chemical analyses (mg/L) for groundwater in the
 645 project area (25/10/08).

Site	Water source	pH	Ca ²⁺	Na ⁺	Mg ²⁺	K ⁺	Fe ²⁺	S[T]
Red Stream (South Ascot)	<u>Bagshot</u> Sand	5.2	22	20	10	5.1	4.4	26
River Bourne (seepage ex Cabrera Trust Land)	<u>Bagshot</u> Sand	5.9	56	27	14	7.4	6.4	25
	Above <u>Bagshot</u> Sand	6.1	40	33	8.0	5.7	0.5	20
River <u>Blackwater</u> (seepage ex <u>Cemex</u> Quarry)	<u>Bagshot</u> Sand	5.6	40	26	9.8	6.5	8.0	46
Spring (<u>Finchamstead</u> Ridges)	Camberley/ <u>Windlesham</u> Sand interface	4.4	24	23	6.1	2.8	1.5	11
Stream (California Country Park)	<u>Bagshot</u> Sand	6.3	27	14	7.9	3.9	5.4	8.1
	Lake above <u>Bagshot</u> Sand	6.4	38	14	6.5	3.9	0.4	10

Table 2. Comparative species analyses for natural (Red Stream, Bracklesham Formation) and industrial (Bullhouse Minewater, Halifax Hard Seam) iron-rich drainage.

<u>Red Stream</u>				<u>Bullhouse minewater</u>			
<u>Cations</u>	Ion equiv.	Anions	Ion equiv.	<u>Cations</u>	Ion equiv.	Anions	Ion equiv.
Al ³⁺	0.01	SO ₄ ²⁻	2.08	Al ³⁺	0.12	SO ₄ ²⁻	15.90
Ca ²⁺	2.45	Cl ⁻	1.41	Ca ²⁺	8.88	Cl ⁻	1.65
Fe ²⁺	0.14	HCO ₃ ⁻	1.00	Fe ²⁺	2.28	HCO ₃ ⁻	1.97
Fe ³⁺	0.03			Fe ³⁺	0.12		
K ⁺	0.16			K ⁺	0.19		
Mg ²⁺	0.66			Mg ²⁺	5.40		
Mn ²⁺	0.01			Mn ²⁺	0.56		
Na ⁺	1.07			Na ⁺	2.09		
Totals	4.53		4.49		19.64		19.42

Fig. 1. Surface distribution of Tertiary sediments in Southern England, adapted from Townsend and Hailwood (1985).

Fig.2. Mapping detail showing northeast draining stream segments superimposed on underlying geology. The segments are coded to indicate modelled ferrous iron concentrations (mg/L Fe^{2+}) based on analytical data rounded to the nearest integer recovered from sampling sites (black dots).

664 Fig. 3. Map of iron contaminated stream water in Berkshire, Surrey and NE
665 Hampshire in relation to underlying geology (simplified from Mason et al., 2010).
666

667
668 Fig. 4. Cross-sections 1 and 2 (ref. Fig. 3) inferred from BGS 1:50000 Geology (Solid
669 and Drift) Sheets 268, 269, 284, and 285 (BGS, 1978, 1999, 2000, 2002).
670

Fig. 5. Geological cross-sections of two drainage channels flowing (1) into and (2) out of Virginia Water Lake, alongside the linearly referenced stream channel data (arrows indicate direction of flow).

Fig. 6. Scatter plots of pH and sulphate concentration versus iron(II).

679

680 Fig. 7. Selected pH values and chemical analyses (mg/L) for the Red Stream from its
 681 source near South Ascot to Virginia Water Lake (21/1/05). Site (and in brackets)
 682 local areas corresponding to each set of analyses are (1) bog (heath) (2) pasture (town)
 683 (3) cultivated grounds (school/homes) (4) pasture (farmland) (5) fen (Silwood
 684 wetland) (6) lake (Silwood Woods) (7) lake (Virginia Water).