

1 Deoxygenated gas occurrences in the Lambeth Group of central 2 London

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10 Abbreviated Title: Deoxygenated Gas in London

11 **Abstract:** Deoxygenated gas poses a serious and life-threatening hazard (confined space hypoxia) for engineering
12 projects in London, particularly those in the Upnor Formation of the Lambeth Group. We review its causes and
13 postulate that it is induced by dewatering or positive pressure tunnelling bringing air into contact with these
14 sediments, causing oxidation. Subsequent resaturation results in pockets of deoxygenated gas. Drawdown of the
15 Lower Aquifer during the industrial growth of London brought air into contact with Lambeth Group sediments on a
16 regional scale. Its recharge has trapped and compressed deoxygenated gas beneath overlying impermeable clays.
17 Historically, the mineral glauconite has been blamed for these hazards, but it lacks potency as a reducing agent and
18 remains unaltered in many oxidised Lambeth Group sediments. Pyrite and organic carbon are both plausible but a
19 more potent agent is green rust, which readily and rapidly oxidises on contact with air, and which is only briefly
20 observed in fresh core samples. This research identifies two key ground engineering hazards: the misidentification of
21 risk by reliance on observations of glauconite; and the likelihood of encountering pressurised deoxygenated gas
22 within Lambeth Group sediments in underground projects following short- or long-term changes in ground water
23 level.

24 Confined space hypoxia (Zugibe *et al.*, 1987), caused by deoxygenated gas, is well-known within
25 the water and sewerage industry and past tragedies have led to increasingly stringent Health and
26 Safety legislation for working in confined conditions underground (Confined Spaces
27 Regulations, 2009). Nevertheless, even with good compliance, hypoxic ground conditions can
28 occur and rapidly lead to unconsciousness and even death. It is therefore imperative for the
29 correct quantification of risk that the conditions under which confined space hypoxia occurs are
30 as well understood as possible.

31 This paper highlights a specific type of confined space hypoxia that occurs within Lambeth
32 Group sediments in central London (Figures 1 and 2), in which deoxygenated but otherwise
33 normal air is encountered underground, often under an excess pressure and occasionally with
34 elevated carbon dioxide.

35

36

37 **1 Background**

38 One of the earliest well-recorded incidents of deoxygenated gas in London tunnelling occurred
39 during construction of the London Underground Limited (LUL) Victoria Line (Morgan and
40 Bartlett, 1969; Clark, 1970), however, the cause of this loss of oxygen was never identified.

41 In 1984 an oxygen-deficient atmosphere was found at the start of each day shift (E. Woods and
42 A. Miller, *pers. comm.*) during construction of the Effra Storm Relief Sewer, south London. The
43 1.83 m internal diameter tunnel was driven beneath Brockwell Park, Dulwich, as a day-works
44 only contract, with the ventilation switched off at the end of each day shift. Oxygen deficiency
45 was encountered at the start of each day shift (with levels restored only after a period of
46 ventilation) through the Streatham Fault Zone (Figure 3), which juxtaposes the London Clay
47 Formation and Lambeth Group sediments, particularly the Upnor Formation, and as a result the
48 ventilation capacity was increased for the remainder of the tunnel drive.

49

50 The most serious incident to date took place in August 1988, when two fatalities occurred during
51 construction of a Thames Water Ring Main (TWRM) shaft at Stoke Newington, north London.
52 The shaft was 46.5 m deep with an 11.9 m internal diameter and had been completed 26 months
53 previously. An engineer and assistant were both asphyxiated within the confined space of a
54 sealed section of pipework extending from a high integrity valve into a closed tunnel heading
55 within the Upnor Formation. It was concluded at the subsequent Crown Court trial (CNPlus,
56 1991) that glauconite, within the soil groundmass, was the probable cause of the hypoxia.

57 Within the same TWRM contract, poor air quality was subsequently encountered during the
58 tunnel drive from Coppermills to this shaft. Internal correspondence from the Resident Engineer
59 (P. Hemmings, *pers. comm.*) noted that air in this section, through the Upnor Formation,
60 contained as little as 11% O₂. A number of construction engineers (E. Woods, G. Howells and A.
61 Miller, *pers. comm.*), working on this section, gave accounts of gas escaping through the final
62 invert of the shaft at Coppermills, visible as bubbles rising vertically through water ponded on
63 the shaft floor. The oxygen-depleted gas was encountered in the section of tunnel in which the
64 invert and base slab were constructed within the Upnor Formation (Figure 4), a section recorded
65 as 'dry' in piezometer data collected. The oxygen deficiency was mitigated through air quality
66 monitoring and adequate ventilation.

67

68 A 'near miss' incident occurred during construction of a cross-passage (C. Warren and E.
69 Woods, *pers. comm.*) between two completed running tunnels of the Channel Tunnel Rail Link
70 (CTRL) beneath Hackney Wick in north London. Another incident took place during caisson
71 sinking of the TWRM shaft at Honor Oak, south London (Newman and Wong, 2011). In both
72 these incidents, an oxygen deficient atmosphere was recorded during construction in the Upnor
73 Formation after a period of dewatering and drawdown from the underlying chalk.

74 Significant oxygen depletion was also recorded within a number of borehole monitoring
75 installations during separate ground investigations for two large tunnelling schemes in north
76 London: Thames Water's North London Flood Relief Sewer (NLFRS); and the TWRM northern
77 extension tunnel.

78

79 During borehole investigations for the section of the NLFRS between Victoria Park and Stoke
80 Newington (Figure 5), samples of gas were taken from borehole installations within the Upnor
81 Formation. Laboratory analyses found that the gas contained up to 98% N₂, less than 1.2% O₂,
82 and elevated levels of CO₂. Rates of gas emission from each borehole were between 1.6 and
83 5.0 m s⁻¹, indicating an over-pressured gas source. Monitoring of the NLFRS site investigation
84 boreholes was undertaken over a 12-month period. The oxygen levels within these installations
85 (also entirely within the Upnor Formation) were consistently below 1% during this time (Figure
86 6), with CO₂ levels between 1 and 2%. Lewis and Harris (1998) proposed a link between these
87 gas levels and barometric pressure but we find no evidence to support such a link in these data.

88

89 Almost the entire 2.82 m internal diameter NLFRS tunnel was driven through the Upnor
90 Formation; given the results of the borehole investigations, clearly defined underground entry
91 procedures and an increased capacity ventilation system were enforced so that no injuries were
92 caused by poor air quality during construction, but gas was frequently heard passing through the
93 tunnel lining (Lewis and Harris, 1998, G. Howells and V. Yuan, *pers. comm.*).

94

95 During site investigation for the extension of the TWRM between Stoke Newington and Thames
96 Water's New River Head (NRH) site in north-central London (Figure 7; Newman *et al.*, 2010),
97 measurements of gas from within borehole monitoring installations in the Upnor Formation
98 indicated up to 2.4% CO₂ and less than 1% O₂ in some of the boreholes. Nitrogen was not

99 measured. Monitoring of the TWRM boreholes was also undertaken over a 12-month period. The
100 oxygen levels (Figure 8) are more variable than the NLFRS data, often with a sharp decrease
101 from a concentration between 12 and 15% to one below 5%, remaining stable at that level
102 thereafter. Again, however, there is no clear link between the gas levels and barometric pressure.

103

104 The 2.85 m internal diameter Stoke Newington to New River Head tunnel was also constructed
105 predominantly within mostly dry Upnor Formation, the interpreted piezometric levels indicating
106 that the stratum lay above the Lower Aquifer.

107 A similar incident was experienced during ground investigation for the Crossrail scheme in
108 London's docklands area, whereby Borehole IOD30R (refer to Figure 2 for location)
109 encountered air escaping from the borehole upon its intersection with the Upnor Formation (U.
110 Lawrence, *pers. comm.*). Subsequent gas monitoring of this indicated significantly low levels of
111 O₂ and slightly elevated CO₂ but no obvious associated effects from changes in barometric
112 pressure.

113 At each of these locations, deoxygenated gas was encountered within the Upnor Formation.
114 However, deoxygenated gas has also been recorded in sandy sections of the Woolwich
115 Formation Laminated Beds at borehole investigations undertaken for proposed residential
116 developments in Romford and Little Ilford, Essex, in 2005 and 2008 respectively (P. Gawne
117 *pers. comm.*), as well as in Thames Water's Tideway Tunnel scheme investigation along a
118 section of the Victoria Embankment (Temple) and in Tower Hamlets in 2009. In these cases the
119 deoxygenated gas was also accompanied by elevated levels of CO₂.

120 At Romford, pockets of air containing severely depleted levels of O₂, at 0.1%, and CO₂ levels as
121 high as 2.6%, were recorded during subsequent monitoring of standpipe installations. At Tower
122 Hamlets, 8.7% O₂ and 0.6% CO₂ were recorded. At both locations drillers recorded 'blowing
123 sand' during borehole excavation and distinct voids were observed in rotary core samples
124 recovered. These are presumed to represent gas migration pathways; material surrounding the
125 voids was noted to be patchily oxidised, although the origin of the gas is unclear at this stage.

126 **2 Causal Mechanisms: Physical Processes**

127 The Upnor Formation is normally considered hydraulically connected with the Chalk via the
128 Thanet Sand Formation, forming the Lower Aquifer of London's water table (Simpson *et al.*
129 1989). In its natural state, prior to any significant human influence, the Lower Aquifer was

130 under artesian pressure (Figure 9), confined throughout much of London by the Lower Mottled
131 Beds above.

132

133 Over-abstraction of the Lower Aquifer began in the early 1800s at rates rising steadily from
134 approximately $9 \times 10^6 \text{ m}^3 \text{ a}^{-1}$ to a peak of $8.3 \times 10^7 \text{ m}^3 \text{ a}^{-1}$ by 1940 (Hurst and Wilkinson, 1986).
135 This led to a significant lowering of the groundwater table and the formation of a large cone of
136 depression beneath west central London, first recognised in 1820 and extensively developed by
137 1850 (Marsh and Davies, 1983). From 1940, the rate of abstraction from the Lower Aquifer
138 reduced significantly with the destruction of a large number of abstraction wells during World
139 War II and the control of abstraction by the 1945 Water Act (Wilkinson, 1985). Escalating costs,
140 the increasing depth of abstraction required, and economic decline limited the number of new
141 wells constructed. Nonetheless, over-abstraction continued until by 1965 the groundwater table
142 had lowered by more than 70 m (lower surface in Figure 9) in the centre of the cone of
143 depression (Simpson *et al.* 1989). This was the lowest level on record and equated to
144 $1.03 \times 10^9 \text{ m}^3$ of water abstracted from more than $1.2 \times 10^{10} \text{ m}^3$ of the Lower Aquifer (Flavin and
145 Joseph, 1983) over an area in excess of 200 km^2 (Marsh and Davies, 1983). The centre of the
146 cone of depression was located close to Charing Cross and Trafalgar Square but a significant
147 area of drawdown occurred within the Lee Valley, near Thames Water's Abbey Mills Pumping
148 Station site.

149 Since 1965, the rate of groundwater abstraction from the Lower Aquifer decreased by between
150 30 and 50%, from $6.2 \times 10^7 \text{ m}^3 \text{ a}^{-1}$ in 1965 to $4.3 \times 10^7 \text{ m}^3 \text{ a}^{-1}$ by 1982 (Wilkinson, 1985). This
151 was allied with the demise of heavy industry, the largest consumer of groundwater, and resulted
152 in a rise in the Lower Aquifer groundwater table. Estimates of the rate of rise vary, from
153 1.5 m a^{-1} (Simpson *et al.* 1989) to 2.5 m a^{-1} (Lucas and Robinson, 1995), to a more recent
154 estimate of 3.0 m a^{-1} (Jones, 2007). The greatest recovery is within the central London cone of
155 depression, which had risen 20 m by 1988 (approximately midway between the 1965 and the
156 pre-abstraction levels in Figure 9). By 1994, the cone of depression had also significantly
157 reduced in geographical extent, becoming confined to an area between Hammersmith and central
158 London, mainly north of the River Thames. Most of the change between lowest recorded levels
159 and highest rate of recovery encompasses an area between Hammersmith in west London and the
160 section of the north bank of the River Thames between Chelsea and Victoria Embankments.

161 By the late 1980s, the continued rise in groundwater level was recognised as a risk to deep
162 tunnels and basements by changing the ground engineering properties and potentially causing

163 flooding. In response, the GARDIT (General Aquifer Research Development and Investigation
164 Team) strategy was launched in 1998 to control the rising groundwater by abstraction of 70 MI
165 per day ($2.56 \times 10^4 \text{ m}^3 \text{ a}^{-1}$) on a schedule up to 2004. However, Thames Water and Environment
166 Agency groundwater modelling demonstrated in 2000 that this rate was too high (Jones, 2007)
167 and should be reduced to 50 MI per day ($1.83 \times 10^7 \text{ m}^3 \text{ a}^{-1}$). Continued monitoring demonstrates
168 the success of GARDIT, with groundwater levels now broadly stable throughout central London
169 (Jones, 2007).

170 The drawdown of the Lower Aquifer is believed (Flavin and Joseph, 1983) to have caused large
171 volumes of permeable saturated Lambeth Group sediments to drain, and air to enter the
172 sediments through 'windows' in the overlying London Clay or via large borehole adits, leading in
173 places to sediment oxidation and the production of deoxygenated air. The GARDIT-controlled
174 incomplete recharge of the Lower Aquifer would then have trapped this deoxygenated air under
175 pressure below impermeable Lambeth Group sediments, in particular the Lower Mottled Beds.

176 The lithologies encountered within the Upnor Formation and adjacent strata are geographically
177 variable but have a broadly consistent stratigraphic sequence (Figure 1). The base of the Upnor
178 Formation is frequently demarcated by a rounded fine to coarse flint gravel, set within a more
179 typical green, clayey, fine to medium sand, with variable quantities of the mineral glauconite
180 (Page and Skipper, 2000). The main body of the Upnor Formation often consists of a grey-green,
181 silty, fine to medium sand to sandy clay, with some fine to medium (occasionally coarse) black
182 flint gravel, commonly containing a variable abundance of the mineral glauconite. In some
183 locations, particularly to the north and east of London and as encountered during the NLFRS and
184 TWRM northern extension, distinct thin to medium interlaminated brown clay and fine sand
185 dominates the unit.

186 The resulting emergence of terrestrial conditions over the area of what is now south east England
187 resulted in the formation of the Lower Mottled Beds (Page and Skipper, 2000). These deposits
188 display characteristically very strong pedogenetic effects, typified by the vivid red, orange and
189 purple hues that are associated with oxidation and other pedogenetic processes within soil
190 horizons (Ellison, 1983). Inspection of numerous borehole core samples and underground
191 excavations across the London area demonstrates that these pedogenetic processes have affected
192 the top of what were formerly Upnor Formation sediments, in particular the gravel that
193 frequently defines the top of this unit (Ellison *et al.*, 1994; Ellison *et al.*, 2004). The lithologies in
194 this zone are distinct from the unaltered material below, comprising an assortment of colours
195 (red, brown, grey and white) of weathered, subrounded, fine to coarse flint set within a light
196 blue-grey mottled orange-brown clay matrix. The effects of pedogenesis diminish with depth,

197 leading to a gradational contact with the unaltered material below, and where permeable they are
198 in hydraulic continuity with the Upnor Formation and the Lower Aquifer.

199 **3 Causal Mechanisms: Chemical Processes**

200 Recharge of the aquifer is a plausible mechanism for the excess gas pressure encountered, as
201 previously deoxygenated air became trapped beneath the Mid-Lambeth Hiatus by impermeable
202 clay-rich layers of the upper parts of the Lambeth Group and the London Clay Formation, but
203 what geochemical reactions are responsible for the reduction of the air trapped in these
204 sediments?

205 Within the construction industry, glauconite is regarded as the reducing agent responsible for
206 loss of oxygen in confined spaces (CNPlus, 1991). Strictly, glauconite is a compositionally-
207 variable series within the mica group and the name is used for all green clay pellets with a
208 glauconitic component (Huggett and Knox, 2006). It has been described (Harder, 1980) as
209 forming within the mildly reducing conditions of cooler (<13°C) deeper marine environments,
210 associated with muddy marine sediments at the interface between reducing and oxidising zones
211 in relatively calm environments with slow sedimentation rates and/or interrupted deposition by
212 precipitation of Fe-hydroxides from Fe, Al, Si and K solutions under reducing conditions.
213 However, the palaeontology and ichnofacies (Skipper, 1999) of the Upnor Formation indicate
214 that it was formed under subtropical shallow marine conditions. Under the binocular microscope,
215 glauconite varies in colour from very pale bluish green to greenish yellow to dark green when
216 fresh. However, when oxidised, it breaks down into iron oxides, displaying a typically brownish
217 yellow or reddish brown colour (Pettijohn *et al.* 1987).

218 During recent borehole investigations for Thames Water's Tideway Thames Tunnel scheme, two
219 boreholes (SR2071 and SA1066D) intersected high pressure ground gas (Newman and Hadlow,
220 2011). Both boreholes were constructed using cable percussion techniques; the first borehole
221 was obtained from a jack-up rig in the River Thames adjacent to Cadogen Pier, Chelsea
222 Embankment; the second from Whitehall Gardens on the Victoria Embankment. In both
223 boreholes, pressurised ground gas was encountered at the point of intersection with the gravelly
224 Lower Mottled Beds, at 50.9 m below river bed level and 56.0 m below ground level
225 respectively. In the case of borehole SR2071, gravel material was ejected to surface, whilst from
226 SA1066D (Figure 9), gas was recorded venting from the borehole casing for a period of eight
227 months until sealed with a permanent cap. A number of return visits were made to this borehole
228 to collect gas samples for laboratory analysis; between 21 August and 15 October 2009 the
229 recorded oxygen content was never more than 3.4% (by volume) and usually less than 2%, with

230 no apparent relationship with barometric pressure. CO₂ was recorded at 600 to 900 ppmv, which
231 at two to three times normal atmospheric concentration is not considered unusual.

232

233 Flow rate observations were not possible until two weeks after gas was first encountered, so the
234 initial rate is uncertain. Assuming an exponential gas release model (Table 1) the initial rate is
235 estimated to have been 120 litres/hour, rapidly declining over a two-week period to a background
236 level determined from long term monitoring of between 7 and 22 litres/hour. This implies that up
237 to 15,500 litres of gas was initially released from a disturbed zone of approximately 2 m radius
238 around the borehole and that up to 500,000 litres was released in total over a 2½ year period. The
239 soil matrix permeability, $\approx 10^{-6} \text{ m s}^{-1}$, inferred from the background rate indicates that a fine silt
240 and clay matrix controls gas migration through this layer.

241

242 Both boreholes SR2071 and SA1066D lie within the (1964) central cone of depression in the
243 Lower Aquifer. Whatever the chemical process, it is clear that a large volume of Upnor
244 Formation could have been oxidised as a result of this cone of depression. However, the
245 subsequent water table recovery was also greatest here and we propose that the rise in the
246 groundwater table since 1965 has trapped and compressed N₂-rich, O₂-depleted gas against the
247 underside of the overlying impermeable clays of the Lower Mottled Beds.

248 As much as 14 km of drilling samples have been recovered to date during the ground
249 investigation for Tideway Thames Tunnel. In a number of instances, examples of apparently
250 fresh (unoxidised) glauconite have been observed within pedogenetically altered sediments
251 belonging to the Lower Mottled Beds (Figure 10), which have been subject to intense
252 weathering, and/or within core samples of the Upnor Formation left exposed to free air over a
253 number of months. This implies that the oxidation of glauconite is not a rapid process and that
254 its decomposition above the water table might not make it the primary culprit in the production
255 of trapped hypoxic gas.

256

257 Obvious alternative reducing agents are organic carbon and pyrite. Organic carbon in the form of
258 driftwood fragments is present throughout the Group, often as dispersed small particles but
259 sometimes in large concentrations. Oxidation of organic carbon primarily results in the
260 production of CO₂. Pyrite is common in the Laminated Beds of the Woolwich Formation and in
261 the Upper Mottled Beds Sand Channel of the Reading Formation, usually as disseminated fine
262 sand grade material or rarely as gravel-sized lumps. Its oxidation leads to acidified groundwater

263 that reacts with any carbonate, ultimately releasing CO₂. The oxidation of both organic carbon
264 and pyrite should therefore be associated with elevated CO₂ levels. Elevated CO₂ levels are
265 sometimes associated with incidents of confined space hypoxia, such as at Thames Water NRH
266 and at Romford, where organic carbon was also noted to be present, but usually the hypoxic gas
267 is 'normal' air with reduced oxygen. Geochemical tests in the Upnor Formation (Table 2), in
268 which many of the incidents occurred, show that pyrite is extremely rare and organic carbon
269 present at very low levels (<1%), typically in the form of isolated wood fragments.

270

271 Fresh core samples from the Upnor Formation and Lower Mottled Beds are frequently observed
272 to have a transient bright bluish green colour (Figure 11) that on exposure to air rapidly changes
273 over a period of minutes to hours to a dull grey-green colour and then, over a few hours or days,
274 to a yellow-orange colour. These changes are characteristic of the oxidation of green rust
275 minerals (Christiansen *et al.* 2009; Taylor and McKenzie, 1980), a reaction that is both much
276 more rapid than glauconite oxidation and one which consumes much more oxygen, weight for
277 weight.

278

279 Green rust is a family of mixed Fe(II) and Fe(III) layered double hydroxides with a pyroaurite-
280 like structure consisting of alternating positively charged Fe(II)/Fe(III), brucite-like, hydroxide
281 layers and hydrated interlayers composed of anions and water molecules (Nagata, *et al.* 2009;
282 Christiansen *et al.* 2009; O'Loughlin *et al.* 2007). It is characteristically bluish-green in colour
283 (Trolard and Bourrie, 2006; Legrand *et al.* 2004), forming in environments close to the
284 Fe(II)/Fe(III) transition zone, in conditions without much oxygen. It forms as free colloidal-size
285 particles within natural groundwater, under weakly acidic to alkaline conditions, and possesses a
286 ratio of Fe(II) to Fe(III) of 2:1 (Zegeye *et al.* 2005). Although chemically distinct, it plays a
287 similar role to that of ferric brown rust in forming a stain or coating on mineral grains in the
288 sediment.

289 Green rust is suspected to be a very common mineral, widely distributed in soils and sediments at
290 a depth of a few metres within certain marine environments and in waterlogged anoxic gley soils
291 (Genin *et al.* 2005). Dissimilatory iron(III)-reducing bacteria (DIRB), in particular *Shewanella*
292 *putrefaciens* (O'Loughlin *et al.* 2007), are metabolically most active in these environments
293 (Parmar *et al.* 2001) and form green rust through the bioreduction of Fe(III) oxides and
294 oxyhydroxides.

295 Green rust crystals are very small, typically about 10 nm across and 3 nm thick, and so possess a
296 relatively high surface area that makes them particularly susceptible to oxidation. The Fe(II)
297 ions oxidise to Fe(III) ions, transforming the green rust to iron oxihydroxides and iron oxides,
298 i.e., the commonly observed brown rust, such as goethite, lepidocrocite and magnetite (Nagata *et al.*
299 *al.* 2009; Trolard and Bourrie, 2006; O'Loughlin *et al.* 2007). Ferrihydrite usually forms only as
300 an intermediate product but may be observed when oxidation is so rapid that alteration to
301 goethite and lepidocrocite does not occur (Refait *et al.* 2003).

302 Some simple calculations demonstrate the potency of green rust with respect to glauconite and
303 other possible reducing agents. Oxidation of 1 kg average glauconite (Bentor and Kastner, 1965)
304 consumes just 6.5×10^{-4} kg O₂. Assuming a gas pressure of 500 kPa (slightly above hydrostatic
305 conditions at 40 m depth), 35% average porosity (this study), dry conditions and normal air
306 composition (21% O₂), each cubic metre of Upnor Formation sediments has up to 2.35 kg free
307 (gaseous) O₂ before reduction. The total mass of material in 1 m³ of Upnor Formation is 1690 kg,
308 assuming a particle density of 2600 kg m⁻³ and 35% porosity. Each cubic metre therefore
309 requires up to 3615 kg, i.e., 213.9 wt% (Table 3), of glauconite to fully reduce this oxygen. Such
310 calculations demonstrate that glauconite cannot be solely or even principally responsible for the
311 loss of oxygen in underground confined air spaces.

312

313 Organic carbon and pyrite are both very powerful reducing agents, respectively requiring
314 just 0.88 kg and 4.4 kg per cubic metre of ground. Both are present in the ground in sufficient
315 quantity but are concentrated into widely dispersed particles with very low reactive areas. Their
316 potency is thus much reduced by permeability and surface area to volume constraints. In
317 addition, there is no evidence from incidences within the Upnor Formation of elevated CO₂ or
318 acidified groundwater that are expected by-products from the oxidation of these materials.

319 Although green rust has a very wide compositional range, measurements by Feder *et al.* (2005)
320 indicate that in a typical ground profile, the average composition is 27% Fe(OH)₂, 62% Fe(OH)₃
321 and 11% Mg(OH), so that 105.3 kg is required per cubic metre of ground, and leaves no
322 characteristic oxidation by-products. Green rust forms as a coating on quartz grains (much like
323 the normal rust that turns sand grains red). These grains are typically silt to sand size, so
324 assuming spherical grains with an average diameter of 0.1 mm and a green rust density of
325 3670 kg m⁻³, 6.2 wt% green rust would form a 1.2 μm thick coating on each quartz grain, giving
326 green rust a remarkably large reactive area. These factors make green rust a strong candidate for
327 primary chemical cause of deoxygenated ground gas in Upnor Formation sediments.

328 **4 Green Rust Detection and Analysis**

329 We hypothesise that the extremely wide distribution of green rust minerals on the surface of
330 sediment grain, coupled with its extreme reactivity and reduction potential, its absence in all but
331 the freshest of core samples make green rust the most likely chemical cause of deoxygenated gas
332 in central London. Furthermore, the absence of green rust and the presence of brown rust in
333 Upnor Formation sediments from cores taken within the lower aquifer cone of depression,
334 indicate that large volumes of sediment in central London may have been oxidised in the last
335 ~150 years, leaving behind a nitrogen-rich hypoxic gas, now pressurised by recharge of that
336 aquifer.

337 A full programme of laboratory testing on borehole samples recovered during the ground
338 investigation phase of the Tideway Thames Tunnel project is underway to identify the
339 mineralogy of reduced and oxidised soil samples. So rapid is the oxidation of green rust that its
340 recovery from field samples for testing is extremely difficult. Samples recovered to date do
341 contain glauconite and goethite (a possible oxidation product of green rust) but green rust itself
342 has not yet been observed, other than briefly by eye during sample recovery. Part of the reason
343 for this may be sample retrieval and preparation. At present the procedure is that immediately
344 following recovery from the ground and while still within a protective, rigid plastic lining, the
345 100 mm diameter core is cut into 100 mm length samples at predetermined intervals within the
346 stratigraphic sequence. Liquid wax is poured onto the open ends of the cut core to form an
347 impenetrable barrier against potential oxidising effects and then wrapped in a layer of cling film.
348 Plastic caps are placed on both ends and then the whole sample is wrapped in a second layer of
349 cling film, labelled and placed within a clear plastic soil sample bag sealed with tape. This
350 procedure is undertaken as rapidly as possible to minimise exposure of the soil sample to
351 oxidation. Nonetheless, when the sample is unwrapped in a specially designed anaerobic
352 chamber (glove box) a measurable increase in oxygen levels is recorded, implying that the
353 waxing and wrapping technique is not entirely effective in preventing oxygen from becoming
354 trapped in the wrapping of the sample. To overcome this issue, future core samples will be
355 vacuum packed immediately upon core recovery and then frozen in dry ice.

356 At present the XRD (X-ray diffraction) and FTIR (Fourier Transform Infrared) analyses cannot
357 be undertaken in an oxygen free environment, with the result that all samples are oxidised during
358 testing. In future, samples will be mixed with glycerol, which acts a barrier against oxidation
359 (Hansen, 1989) without unduly affecting the analyses. Normal powder X-ray diffraction
360 techniques dehydrate the green rust before testing, XRD-PSD (Position-Sensitive Detector) is
361 capable of 'real time' analysis and is being used alongside infrared spectroscopy to characterise

362 the reactants and reaction rates of the samples on exposure to air. It is hoped that these measures
363 will allow quantitative identification of green rust in the recovered core samples.

364 **5 Conclusions**

365 This study has identified two key hazards for geotechnical engineering in Lambeth Group
366 (particularly Upnor Formation) sediments in London: the misidentification of the risk of
367 confined space hypoxia by reliance on observations of glauconite; and the likelihood of
368 encountering pressurised deoxygenated, nitrogen-rich gas following short- or long-term changes
369 in ground water level.

370 Glauconite should no longer be considered the most important predictor for confined space
371 hypoxia and the absence of glauconite should not be taken to imply a lower risk of its incidence.
372 Lambeth Group geology is complex and different factors appear to be important in different
373 locations/stratigraphic depths but our research to date strongly suggests that other minerals, such
374 as green rust, pyrite and organic carbon, have a much more important role in the occurrence of
375 confined space hypoxia. While pyrite and organic carbon are relatively easy to identify and may
376 leave a characteristic signature following oxidation, to date green rust has proved particularly
377 difficult to identify, even in samples collected specifically for this research project. In very fresh
378 samples (such as while drilling or boring) green rust can be identified by its characteristic teal
379 (blue/green) colour, but its rapid oxidation requires that such observations be made within the
380 first few minutes of sample extraction.

381 Current and past dewatering pose significant risks, potentially causing the build up of
382 deoxygenated gas under pressure following a rise in water level. The limited gas flow data
383 collected to date indicates that the permeability of gas in Upnor Formation sediments is similar to
384 that of water, i.e., $\approx 10^{-6} \text{ m s}^{-1}$. Under these conditions, a single borehole would take almost a year
385 to relieve the gas pressure in soil out to a 30 m radius, and thus it is most likely impractical to
386 relieve any excess gas pressure encountered within an engineering project. While this may not be
387 an immediate concern for pressure-balancing tunnel boring machines (TBMs), oxygen-poor gas
388 may readily seep through some concrete tunnel linings, particularly during the first year of
389 installation (Pihlajavaara, 1991), posing a hazard to personnel during fitting out or inspection
390 work. Indeed, the high forward ground pressures induced by pressure-balancing TBMs may
391 exacerbate this problem.

392 Further research into this hazard is urgently required to identify structural and lithological
393 controls on the migration and trapping of hypoxic gas and to develop a rapid, reliable and
394 quantitative technique for the identification of green rust in fresh or properly preserved samples.

395 The authors welcome contact from drillers, engineers, geologists and anyone else with
396 experience of encountering hypoxic conditions, pressurised anoxic gas, or elevation CO₂ levels
397 on site. Confidentiality will be respected.

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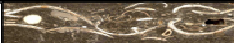





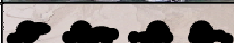
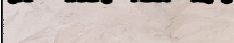

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- 107

FORMATION	Member / Beds	Description	Appearance
LONDON CLAY	N/A	Silty to slightly sandy CLAY	
HARWICH	Swanscombe	Sandy shelly CLAY	
	Oldhaven	Clayey GRAVEL / SAND	
WOOLWICH	Upper Shelly Beds	Shelly CLAY	
READING	Upper Mottled Beds	Blue grey mottled sandy CLAY	AQUICLUDE
WOOLWICH	Laminated Beds	Laminated fine sandy CLAY	
	Lower Shelly Beds	Shelly CLAY	
READING	Lower Mottled Beds	Blue orange red mottled CLAY with sand and gravel	AQUICLUDE
UPNOR	N/A	Clayey SAND with gravel	Deoxygenated gas under pressure
THANET SAND	N/A	Silty fine SAND –clayey towards base	
	Bullhead Bed	Clayey, sandy flint GRAVEL	
SEAFORD CHALK	Haven Brow	Mod weak to weak white CHALK	
	Cuckmere		
	Belle Tout		

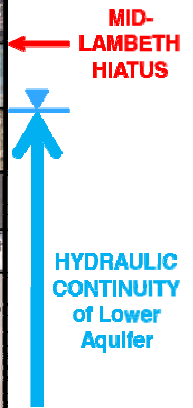


Figure 1. The geological succession for London, with details of variations within the Lambeth Group. Deoxygenated gas incidences are primarily known from the Upnor Formation but are also known from the Laminated Beds.

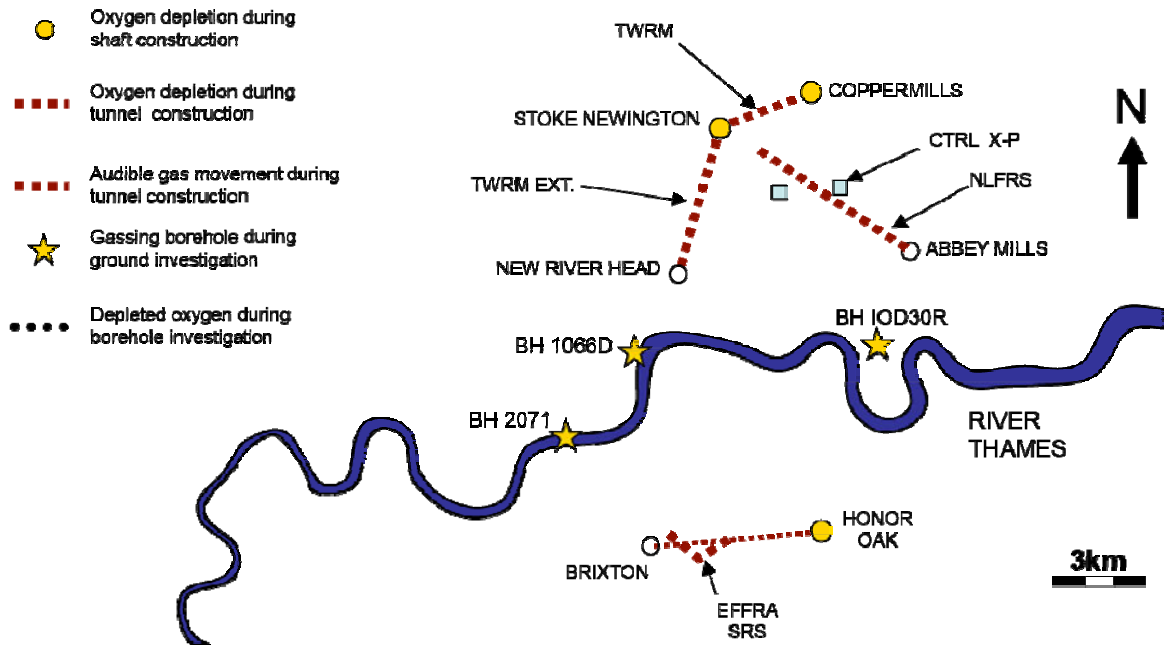


Figure 2. Location map of ground gas incidences during construction.

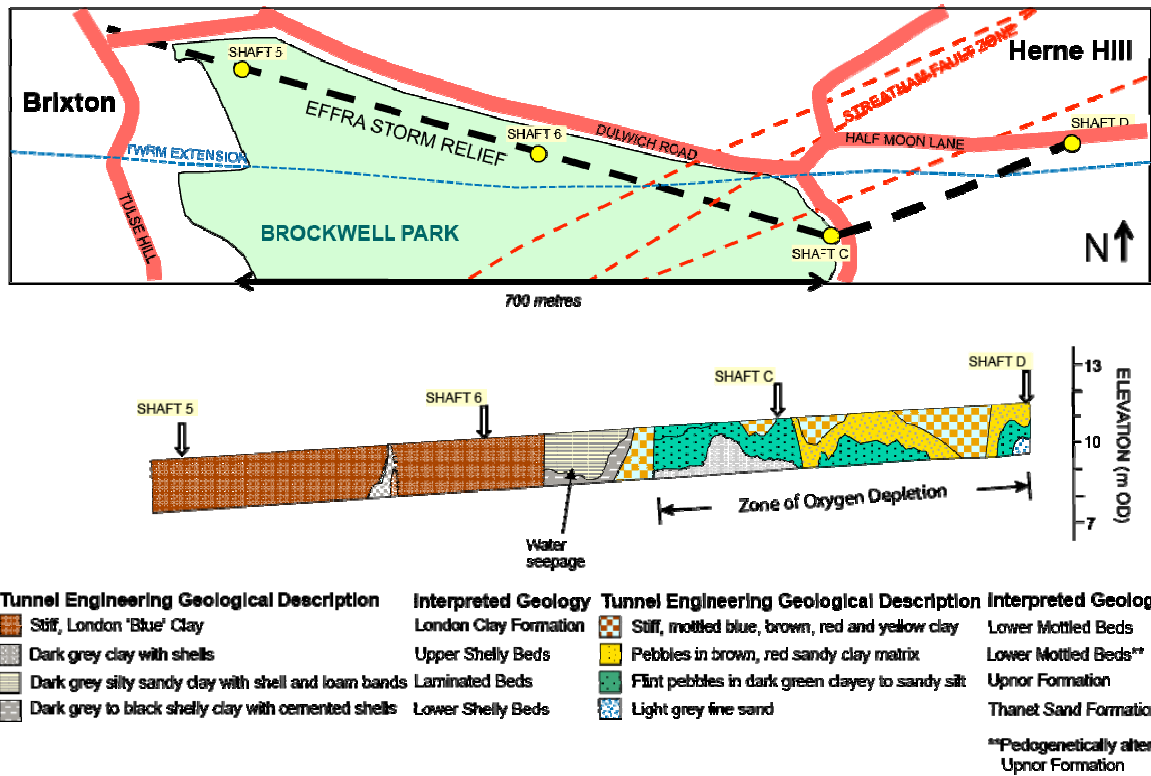
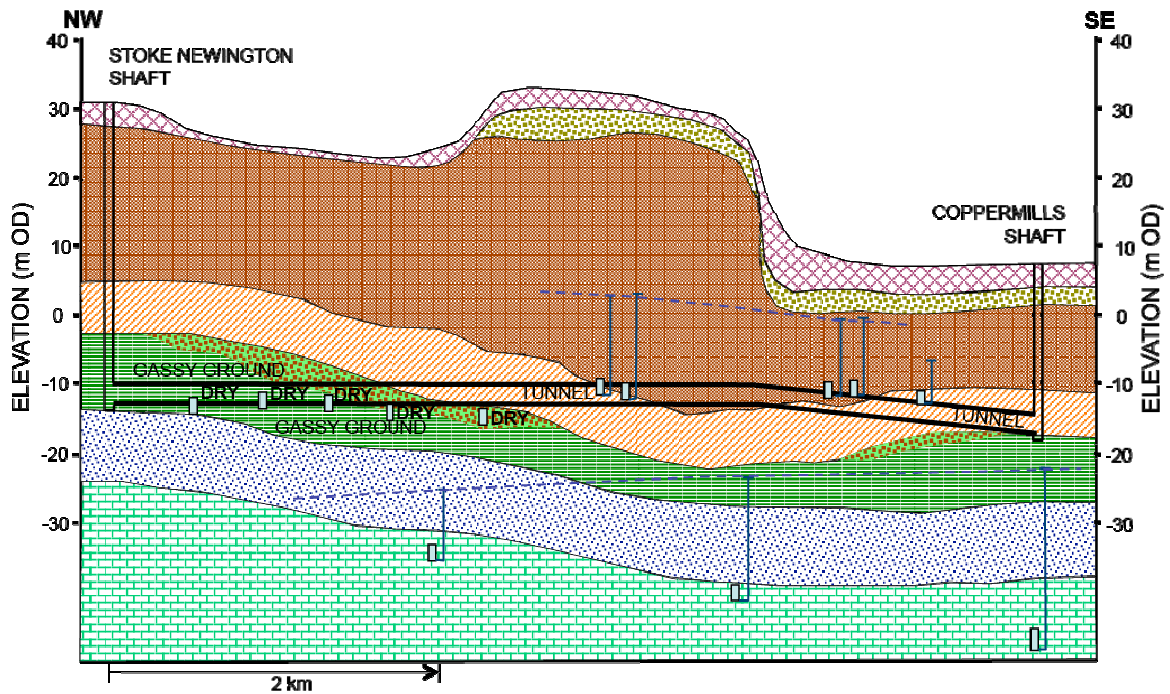


Figure 3. Schematic geological section along the Effra storm relief sewer.



KEY TO GEOLOGY AND SYMBOLS IN FIGURES 4, 5 AND 7

- | | | |
|---|------------------------|-----------------------|
| MADE GROUND & ALLUVIUM | RIVER TERRACE DEPOSITS | LONDON CLAY FORMATION |
| LAMBETH GROUP (EXCL. UPNOR FORMATION) | LOWER MOTTLED BEDS | UPNOR FORMATION |
| GRAVELLY UPNOR FORMATION | THANET SAND FORMATION | WHITE CHALK SUBGROUP |
| GEOLOGICAL FAULT (WITH THROW) | | |
| INTERPRETED PIEZOMETRIC LEVEL | BOREHOLE | |
| POSITION OF BOREHOLE MONITORING INSTALLATION AND WATER LEVEL RISE | | |

Figure 4. Schematic geological section between Coppermills and Stoke Newington.

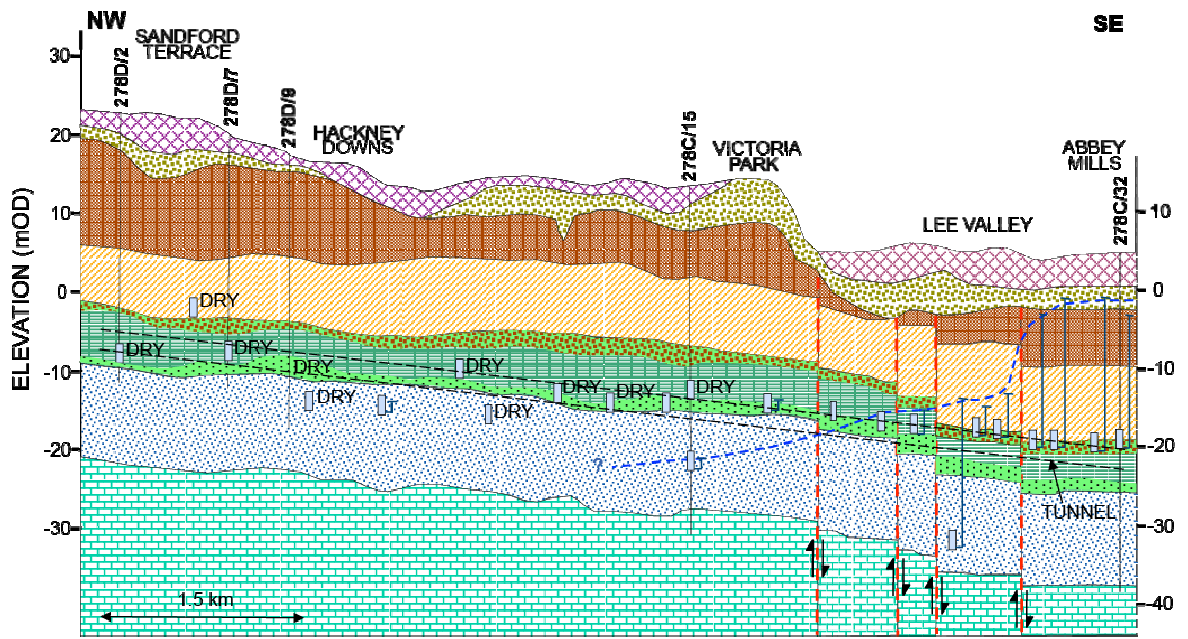


Figure 5. Schematic geological section between Stoke Newington and Abbey Mills. Refer to Figure 4 for key.

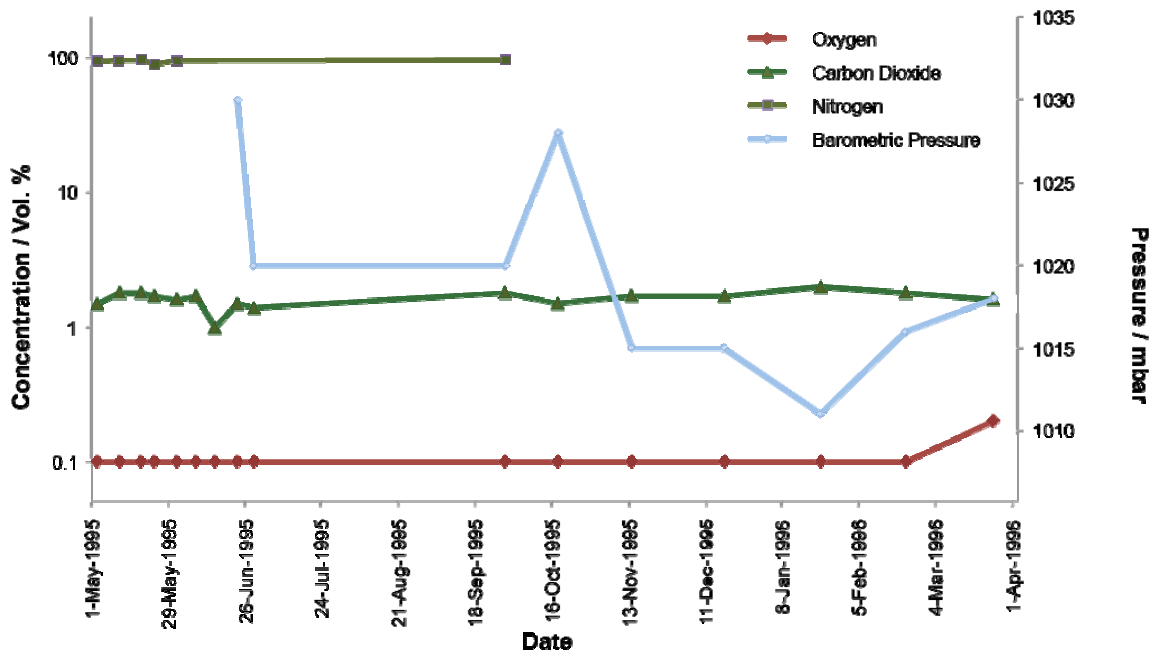


Figure 6. Monitored gas levels in North London Flood Relief Sewer borehole 278D

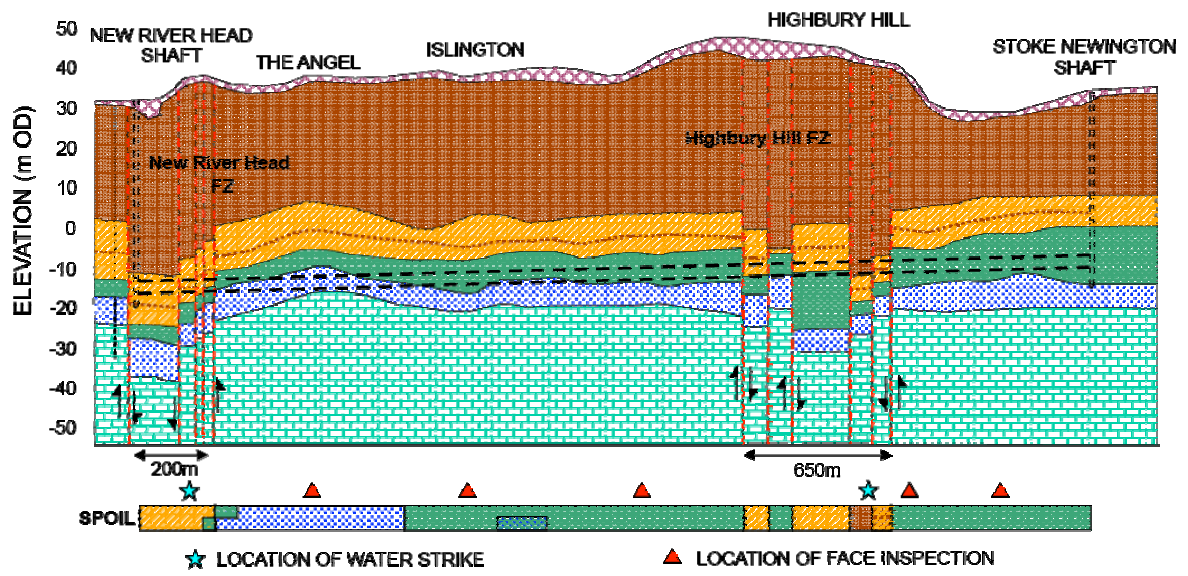


Figure 7. Schematic geological section between Stoke Newington and New River Head (from Newman et al., 2010). Refer to Figure 4 for key.

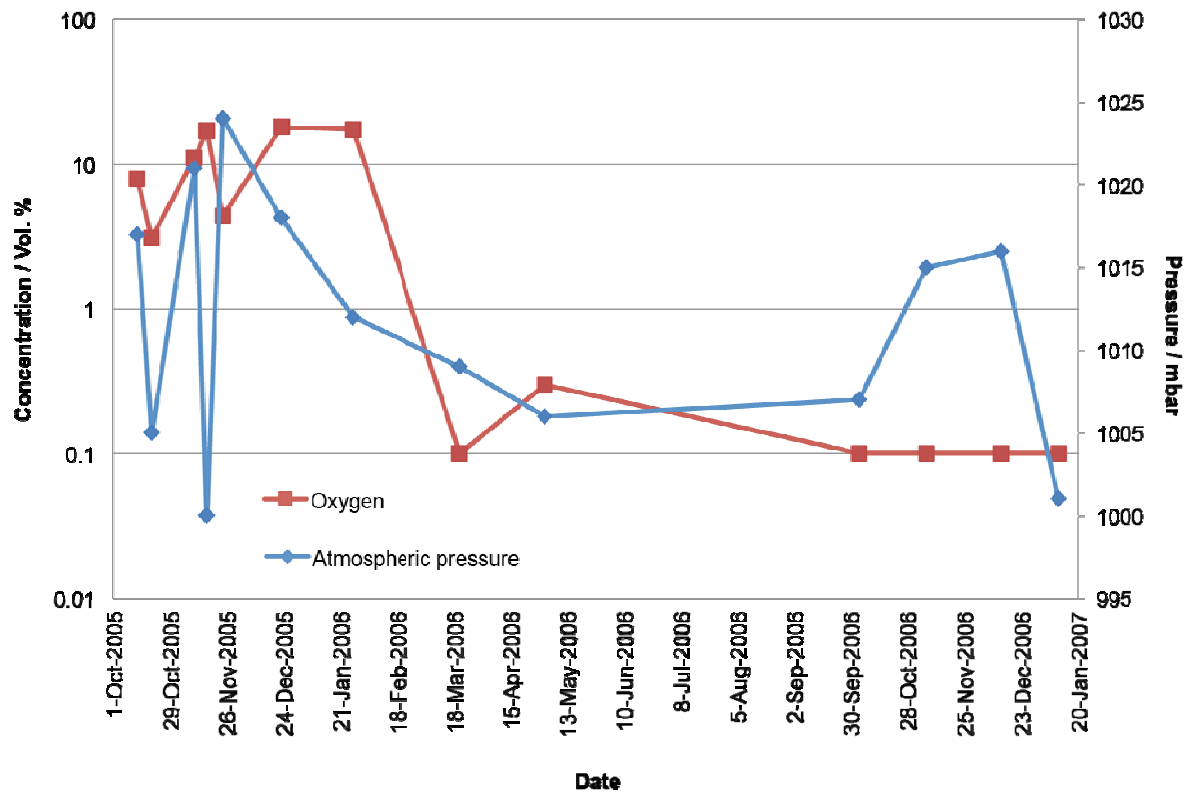


Figure 8. Monitored gas levels in TW New River Head borehole 773A.

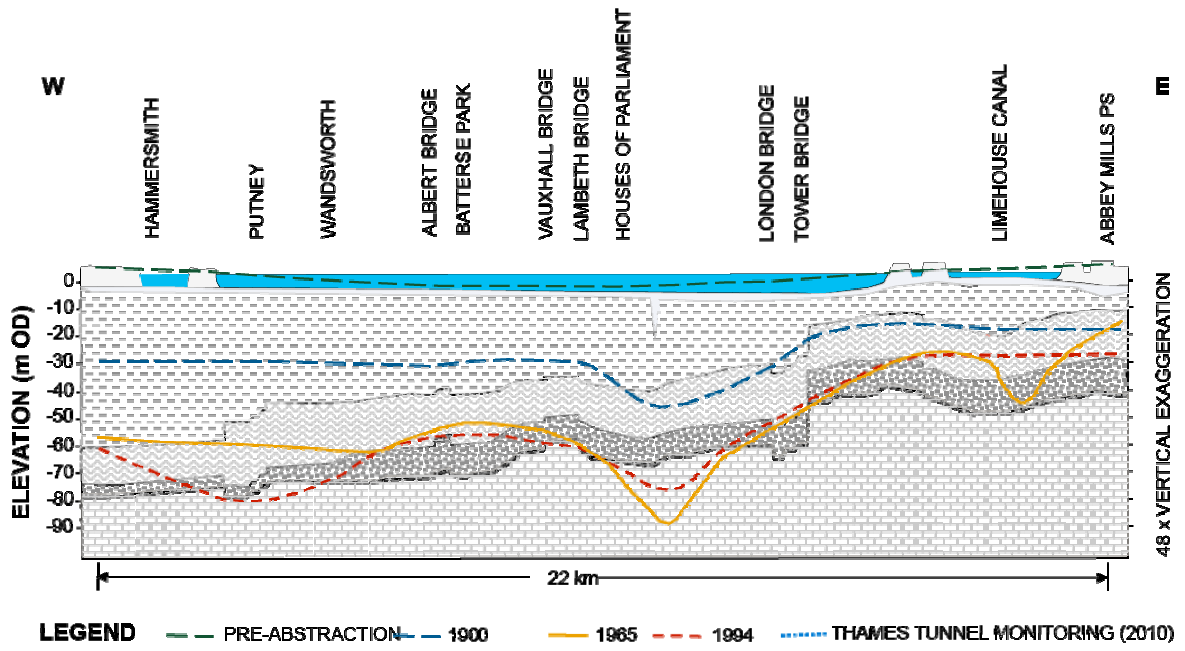


Figure 9. Piezometric levels across London 1800 to 1994.

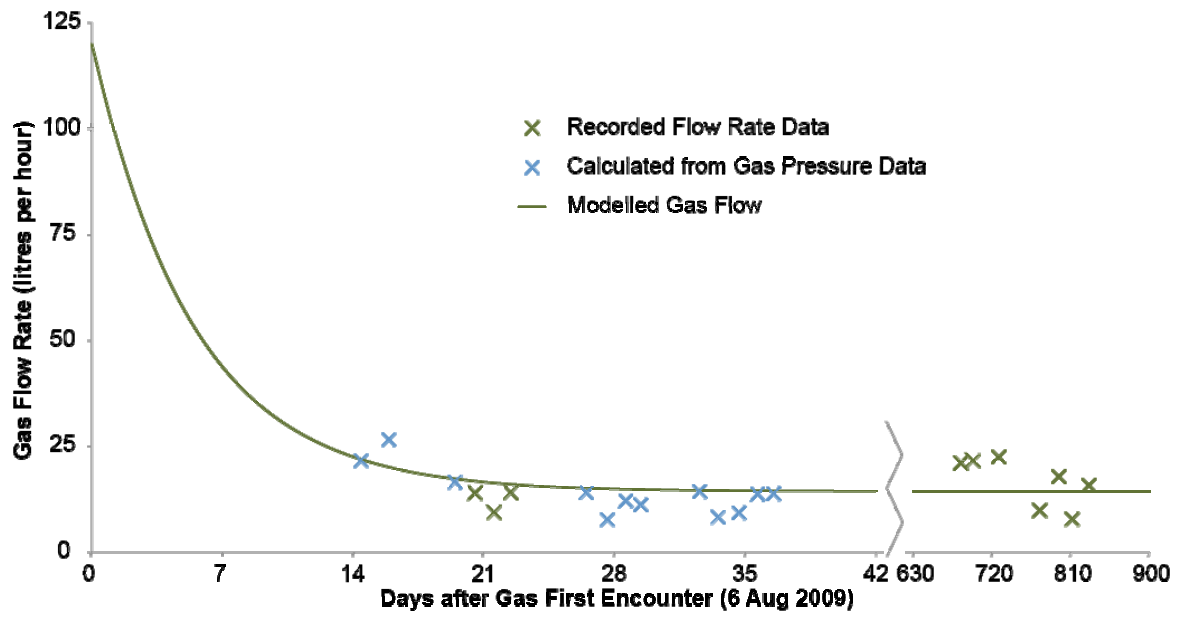


Figure 10. Gas production from borehole SA1066D.



Figure 11.

Sediments of the Lower Mottled Beds illustrating pedogenic alteration and unoxidised glauconite.



Figure 12. Green rust (bluish surface colour) in fresh core samples.

Table 1 Gas Release Model for SA1066D.

Gas Release Model for SA1066D	
Initial Rate of Gas Release	120 litres / hour
Background Rate of Gas Release	14.3 ± 7.3 litres / hour
Total Volume of Gas released from Disturbed Zone	13.9 ± 1.5 m ³
Thickness of Soil Layer containing Gas	2.5 to 4.0 m
Porosity of Soil Layer	35 to 50%
Radius of Disturbed Zone	1.8 ± 0.3 m
Soil Permeability with respect to Gas Flow	2.3 ± 1.5 × 10 ⁻⁶ m s ⁻¹
Gas Composition	97.6 ± 0.5% N ₂ , 2.4 ± 0.7 % O ₂ , 730 ± 160 ppm CO ₂

Table 2 X-Ray Diffraction Analysis of Lambeth Group Sediments.

Component (wt%)	Glaucouite ¹	Glaucouite ²	Kaolinite	Smectite	Quartz	Goethite	Pyrite ³	Carbonate
Lower Mottled Beds	0.9 ± 3.0	12.5 ± 12.5	7.1 ± 5.5	35.6 ± 26.2	27.3 ± 25.6	4.0 ± 3.9	0.2 ± 0.6	0.3 ± 0.7
LMB Gravels	15.9 ± 17.4	19.7 ± 17.8	1.4 ± 2.2	21.3 ± 16.7	47.3 ± 25.8	3.2 ± 4.6	0.1 ± 0.5	0.7 ± 1.2
Upnor Formation	9.1 ± 6.5	15.9 ± 8.4	1.2 ± 1.8	12.5 ± 8.5	61.0 ± 14.8	0.3 ± 1.0	0.1 ± 0.4	1.1 ± 1.8
Thanet Sands	2.3 ± 2.3	5.4 ± 5.3	0.5 ± 1.0	2.8 ± 5.3	81.6 ± 12.5	0.0 ± 0.0	0.0 ± 0.0	0.3 ± 1.2

¹Point-Count data (vol. %); ²XRD: includes illite and mica; ³includes gypsum. ± is one standard deviation.

Table 3 Potency of Reducing Agents in the Upnor Formation.

Compound	Reducing Potential	Mass Fraction	Grain Size	Reactive Area ⁱ	Required Mass Fraction ⁱⁱ
Glauconite	0.00065 kg kg ⁻¹	15.9 ± 8.4 wt%	0.5 mm	1220 m ²	213.9 wt%
Pyrite	0.80 kg kg ⁻¹	0.1 ± 0.4 wt%	0.1 mm	20 m ²	0.2 wt%
Organic Carbon	2.67 kg kg ⁻¹	<< 0.1 wt%	3 mm	<3 m ²	0.1 wt%
Green Rust	0.022 kg kg ⁻¹	unknown	0.1 mm ⁱⁱⁱ	23,340 m ²	6.2 wt%

ⁱ grain area per m³ of soil; ⁱⁱ to reduce 2.35 kg O₂ per m³ of soil; ⁱⁱⁱ average size of quartz grains coated by green crust.