Mechanisms of metals removal during passive mine water treatment at low and circumneutral pH

SAPSFORD, D.J.[1] FLORENCE, K. [1], BARNES, A.[2]

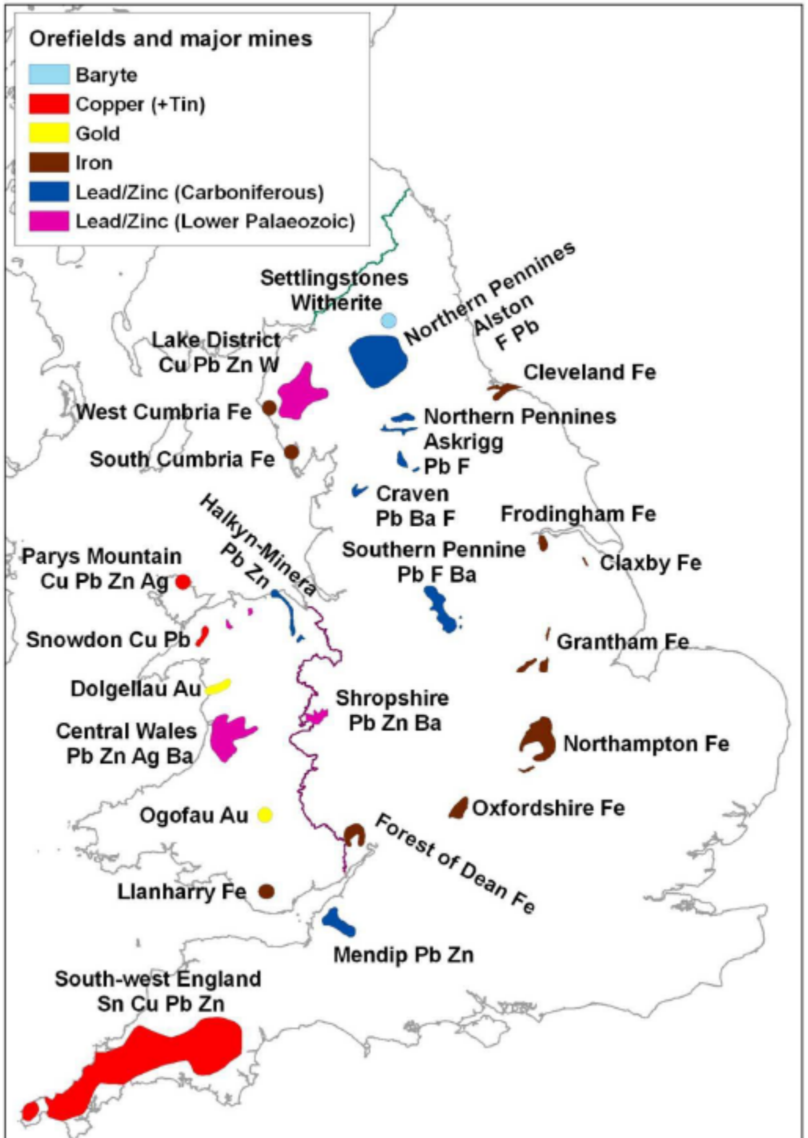
[1]CARDIFF SCHOOL OF ENGINEERING, CARDIFF UNIVERSITY
[2] SRK CONSULTING UK

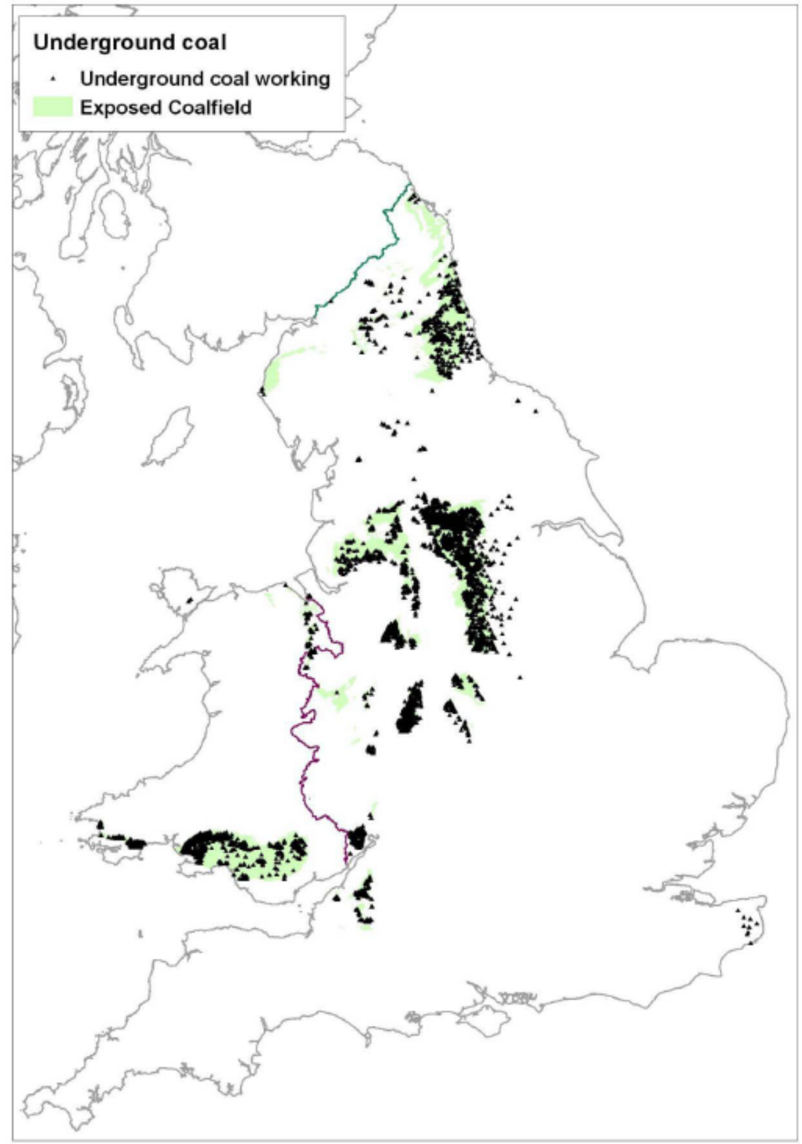
NA H-EILEANAN AN IAR
HIGHLAND
MORAY
ABERDEENSHIRE
ABERDEEN CITY
Dashed lines are for clarification purposes only.
PERTH AND KINROSS
ANGUS
DUNDEE CITY
ARGYLL AND BUTE
STIRLING
CLACKMANNANSHIRE
WEST DUNBARTONSHIRE
EAST DUNBARTONSHIRE
EAST LOTHIAN
NORTH AYRSHIRE
SOUTH LANARKSHIRE
SCOTTISH BORDERS
SOUTH AYRSHIRE
DUMFRIES AND GALLOWAY
SHETLAND ISLANDS
ORKNEY ISLANDS
1 INVERCLYDE
2 RENFREWSHIRE
3 EAST RENFREWSHIRE
4 GLASGOW CITY
5 EDINBURGH CITY
6 LIVERPOOL
7 BOLTON
8 SALFORD
9 TRAFFORD
10 ROCHDALE
11 MANCHESTER
12 TAMESIDE
13 OLDHAM
14 CITY OF WOLVE
15 WALSALL
16 SANDWELL
17 DUDLEY
18 BIRMINGHAM
NEWCASTLE UPON TYNE
GATESHEAD
HARTLEPOOL
REDCAR AND CLEVELAND
DARLINGTON
MIDDLESBROUGH
CUMBRIA
NORTH YORKSHIRE
LANCASHIRE
BLACKBURN WITH DARWEN
London area inset
1 BARKING & DAGENHAM
2 BARNET
3 BEXLEY
4 BRENT
5 BROMLEY
6 CAMDEN
7 CITY OF WESTMINSTER
8 COUNTY OF THE CITY OF LONDON
9 CROYDON
10 EALING
11 ENFIELD
12 GREENWICH
13 HACKNEY
14 HAMMERSMITH & FULHAM
15 HARINGEY
16 HARROW
17 HAVERING
18 HILLINGDON
19 HOUNSLOW
20 ISLINGTON
21 LAMBETH
22 LEWISHAM
23 MERTON
24 NEWHAM
25 REDBRIDGE
26 RICHMOND UPON THAMES
27 ROYAL BOROUGH OF KENSINGTON & CHELSEA
28 ROYAL BOROUGH OF KINGSTON UPON THAMES
29 SOUTHWARK
30 SUTTON
31 TOWER HAMLETS
32 WALTHAM FOREST
33 WANDSWORTH
0 10 km
ISLE OF ANGLESEY
CONWY
GWYNEDD
DERBYSHIRE
CITY OF DERBY
TELFORD AND WREKIN
SHROPSHIRE
RUTLAND
CITY OF PETERBOROUGH
CITY OF LEICESTER
NORFOLK
CEREDIGION
POWYS
WORCESTERSHIRE
NORTHAMPTONSHIRE
CAMBRIDGESHIRE
SUFFOLK
COUNTY OF HEREFORDSHIRE
MILTON KEYNES
BEDFORDSHIRE
LUTON
PEMBROKESHIRE
CARMARTHENSHIRE
MERTHYR TYDFIL
BLAENAU GWENT
MONMOUTHSHIRE
HERTFORDSHIRE
ESSEX
BUCKINGHAMSHIRE
THURROCK
SOUTHEND-ON-SEA
London area (see inset)
NEWPORT
CARDIFF
THE VALE OF GLAMORGAN
SLOUGH
WINDSOR AND MAIDENHEAD
WOKINGHAM
BRACKNELL FOREST
WILTSHIRE
MEDWAY
SURREY
KENT
Welsh spellings
BLAENAU GWENT.....BLAENAU GWENT
BRIDGEND.....PEN-Y-BONT AR OGWR
CAERPHILLY.....CAERFFILI
CARDIFF.....CAERDYDD
CARMARTHENSHIRE.....SIR GAERFYRDDIN
CEREDIGION.....SIR CEREDIGION
CONWY.....CONWY
DENBIGHSHIRE.....SIR DDINBYCH
FLINTSHIRE.....SIR Y FFLINT
GWYNEDD.....GWYNEDD
ISLE OF ANGLESEY.....SIR YNYS MÔN
MERTHYR TYDFIL.....MERTHYR TUDFUL
MONMOUTHSHIRE.....SIR FYNWY
NEATH PORT TALBOT.....CASTELL-NEDD PORT TALBOT
NEWPORT.....CASNEWYDD
PEMBROKESHIRE.....SIR BENFRO
POWYS.....POWYS
RHONDDA, CYNON, TAFF.....RHONDDA, CYNON, TAF
SWANSEA.....ABERTAWE
THE VALE OF GLAMORGAN.....BRO MORGANNWG
TORFAEN.....TOR-FAEN
WREXHAM.....WRECSAM
SOMERSET
HAMPSHIRE
WEST SUSSEX
EAST SUSSEX
DEVON
DORSET
POOLE
CITY OF SOUTHAMPTON
ISLE OF WIGHT
CITY OF PORTSMOUTH
CITY OF BRIGHTON & HOVE
BOURNEMOUTH
TORBAY
CORNWALL
CITY OF PLYMOUTH
0 50 100 km
Boundaries revised to April 2001
© Crown copyright 2001

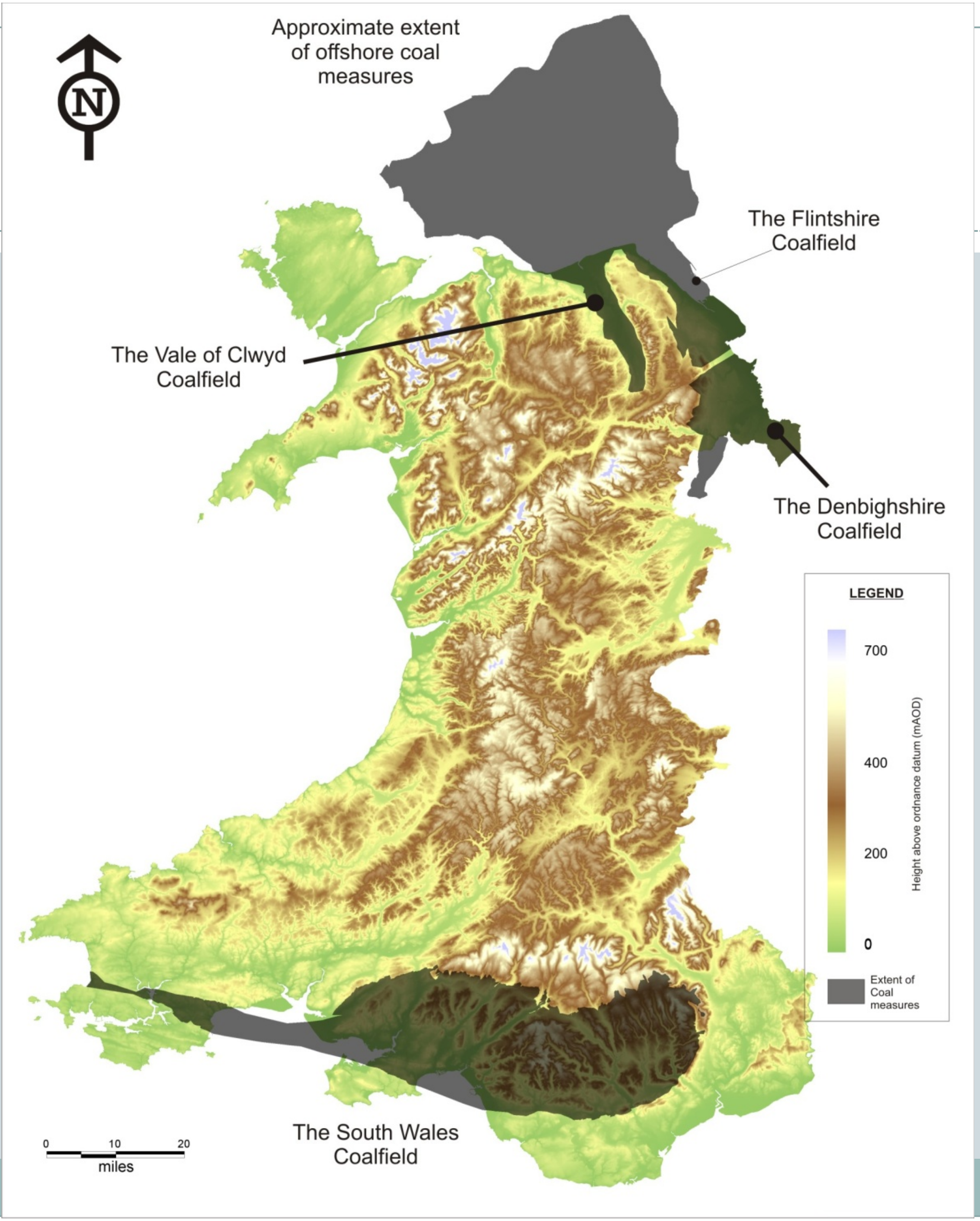
UK Mining

The nature of waste associated with closed mines in England and Wales

Minerals & Waste Programme
Open Report OR/10/14

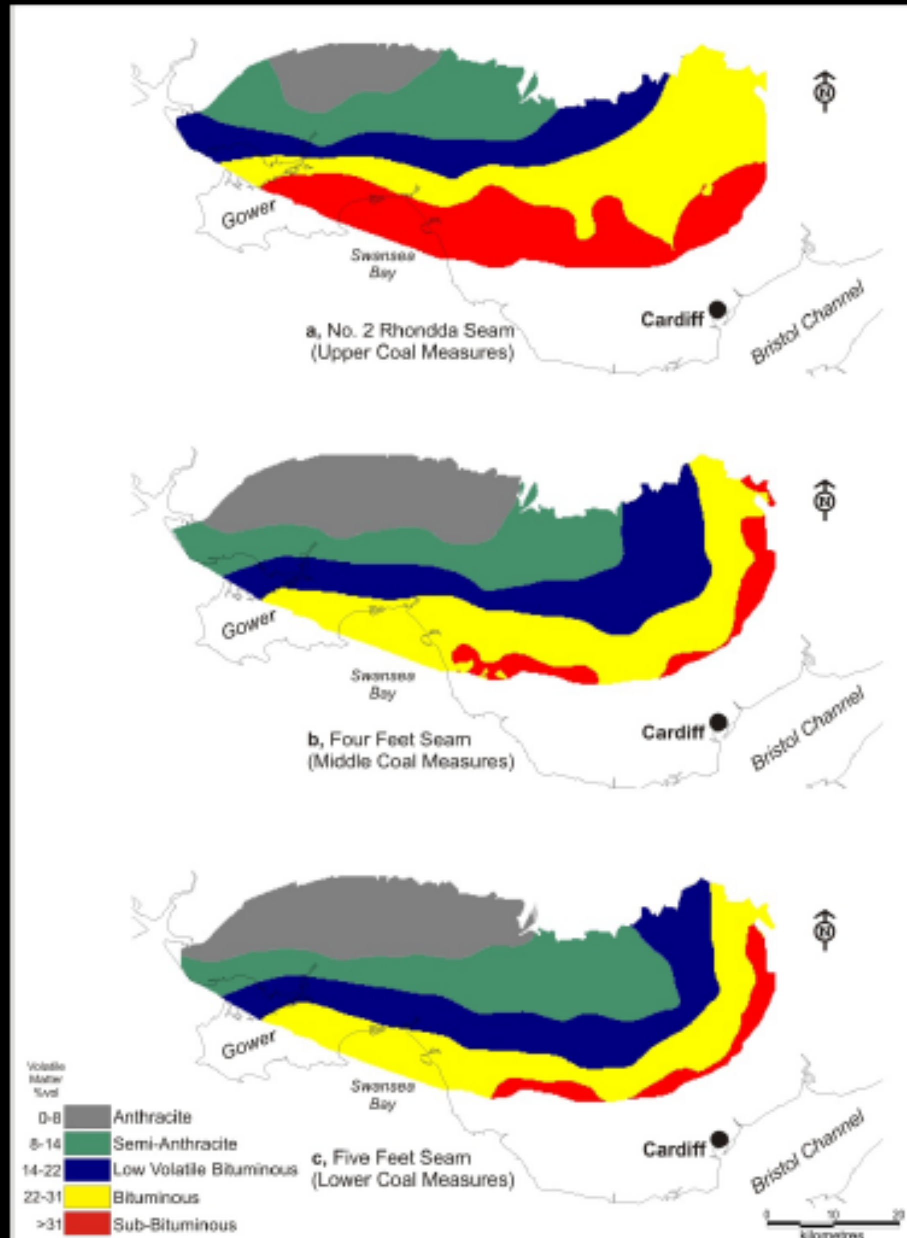




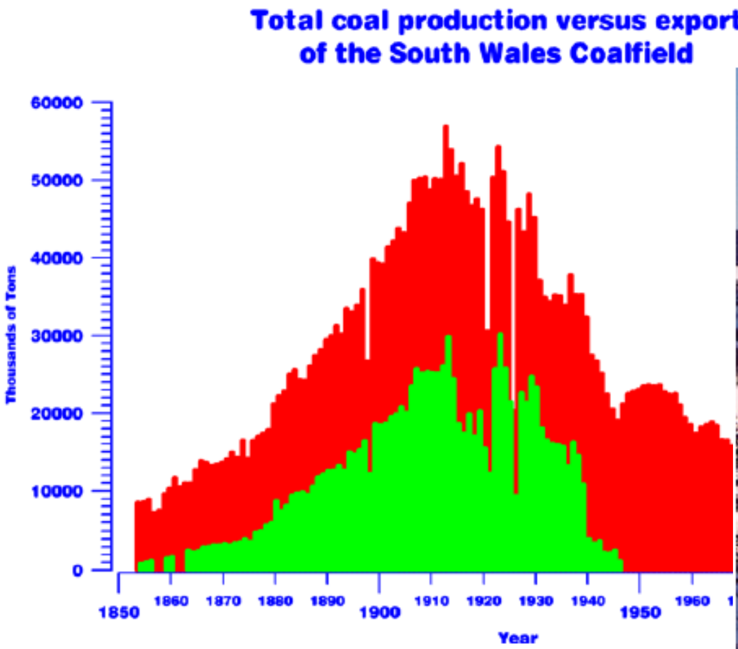

Approximate extent of offshore coal measures
N
The Flintshire Coalfield
The Vale of Clwyd Coalfield
The Denbighshire Coalfield
LEGEND
700
400
200
0
Height above ordnance datum (mAOD)
Extent of Coal measures
The South Wales Coalfield
0
10
20
miles

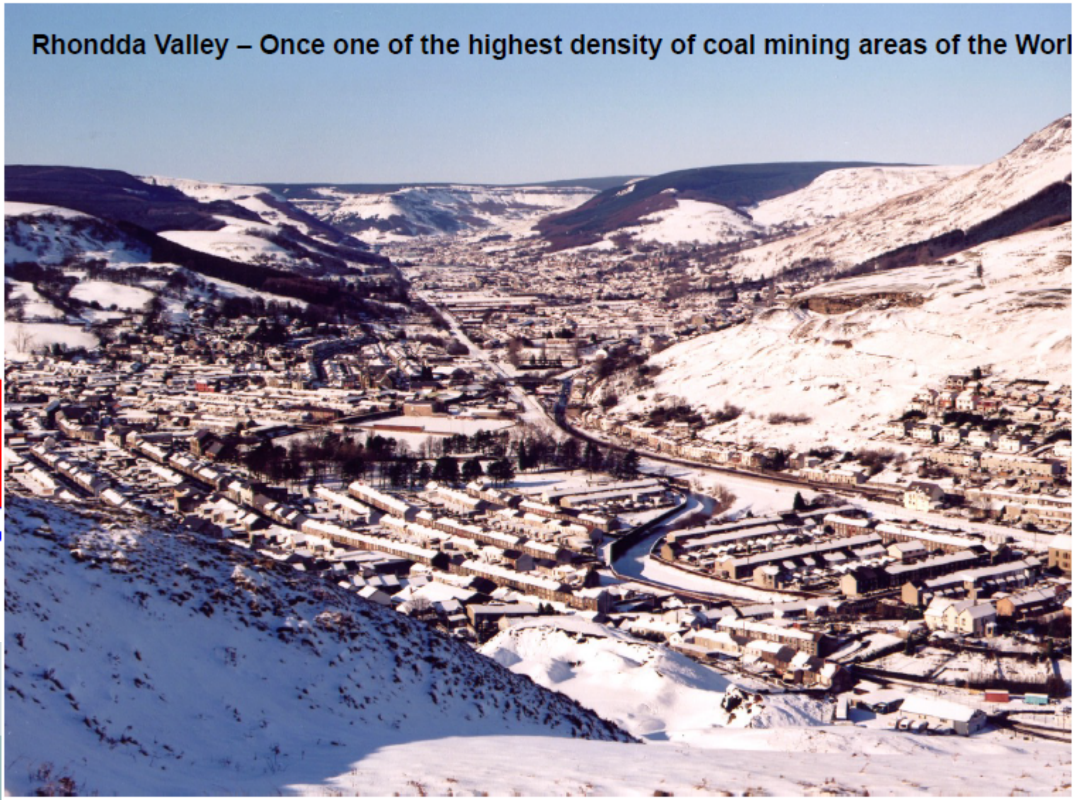
Coal Rank Variation in South Wales

Sub-Bituminous
to
Bituminous
to
Anthracite

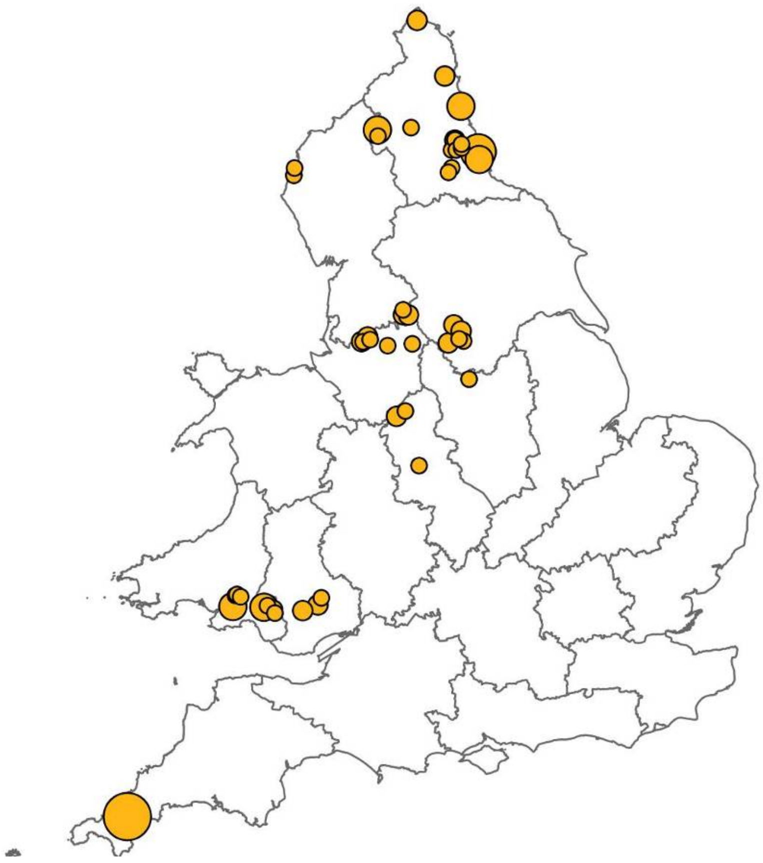


At peak production in 1913over 50% of coal was exported through ports Cardiff, Swansea, Barry & Newport

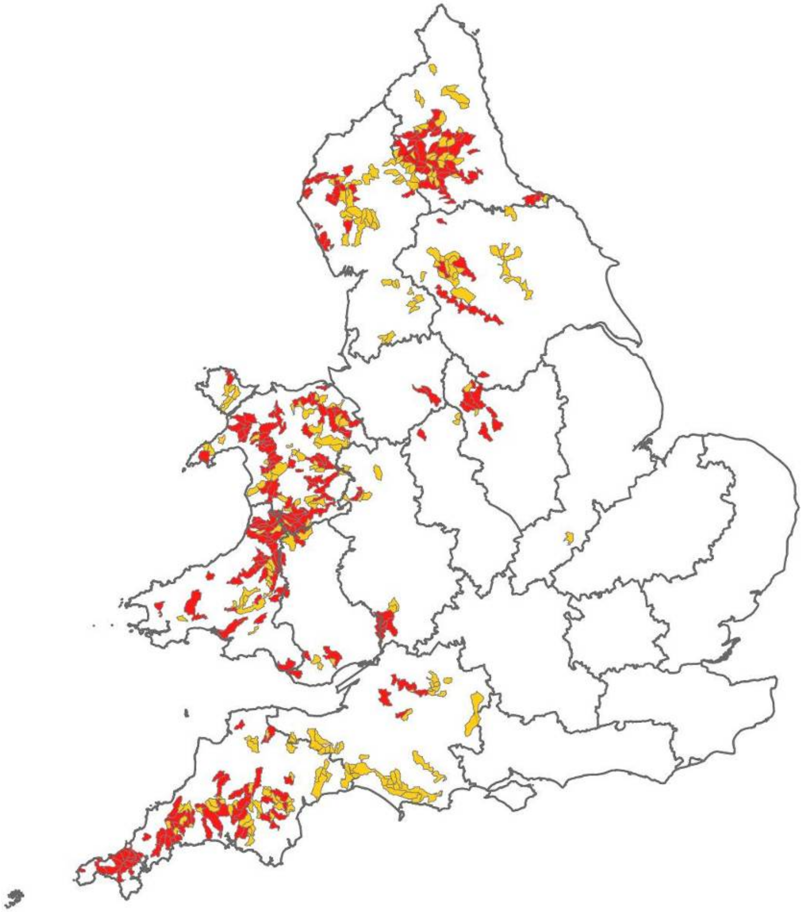




UK mine waters



Coal mine water treatment



Non-coal mine water impacted catchments (EA)

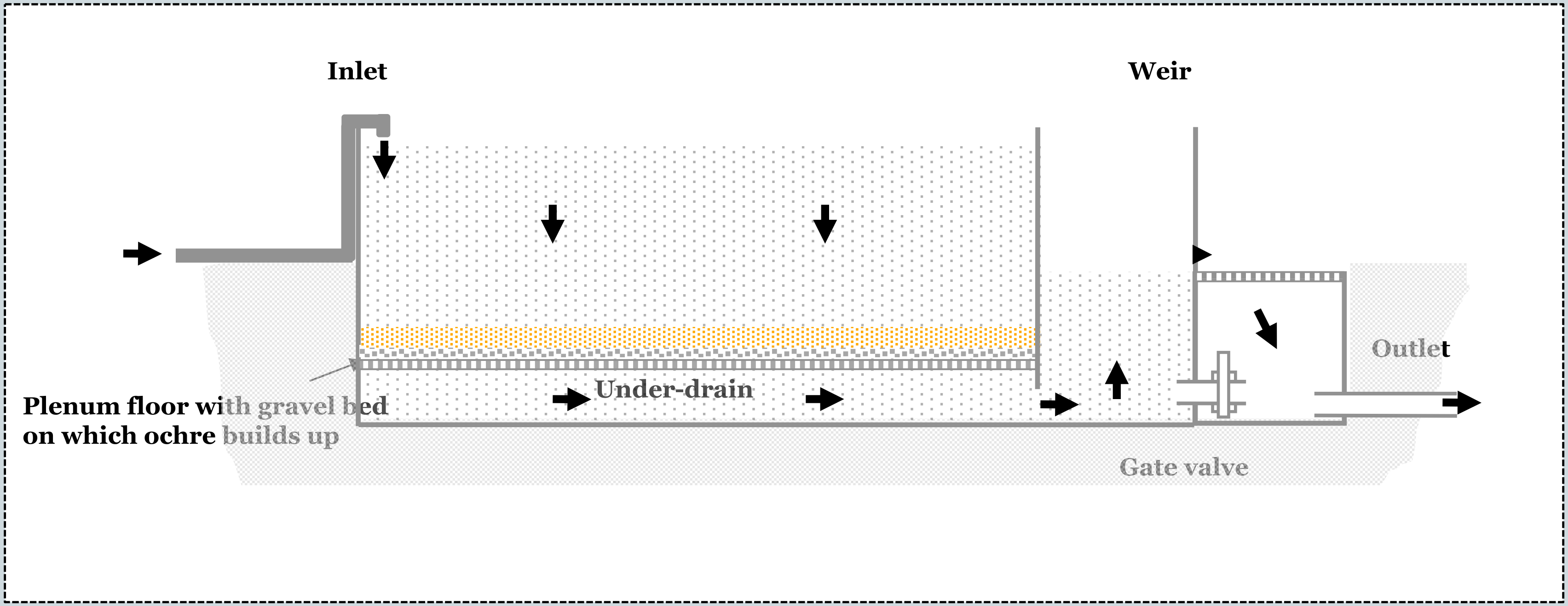

Image taken from google Earth
7
6
1
R 3
R 2
8
5
R 1
L 1
2
4
L2
3
20m
Image taken from google Earth
1
L2
2
L1
3
R1
R2
R3
5
4
6
20m


Drivers for Research
[1] Land Availability
[2] Ochre Recovery

Whitworth ‘A’ RAPS, Tonmawr

The Pilot Tank

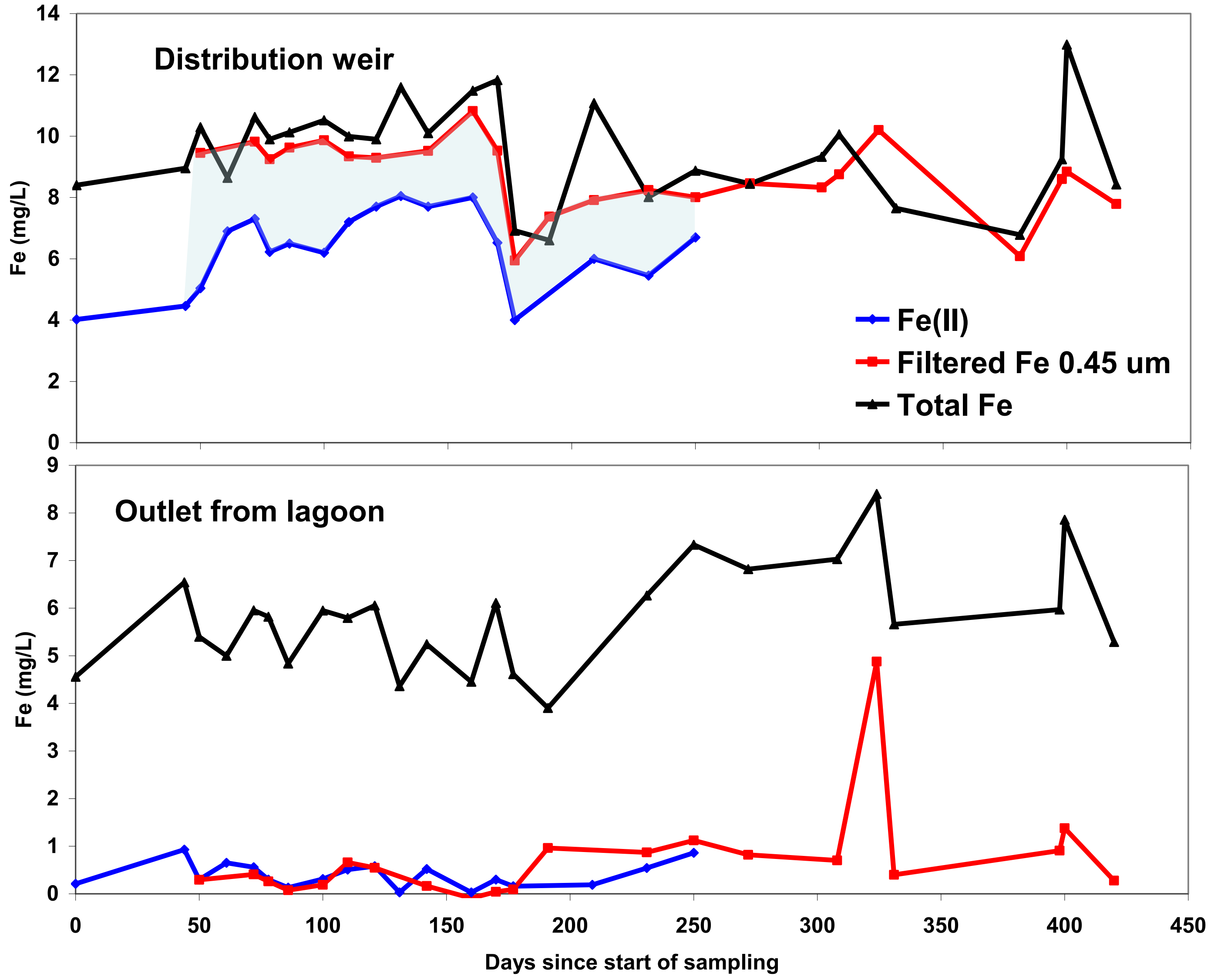
Enhanced iron removal by (self) filtration of ochre particles and surface-catalysed oxidation of dissolved iron



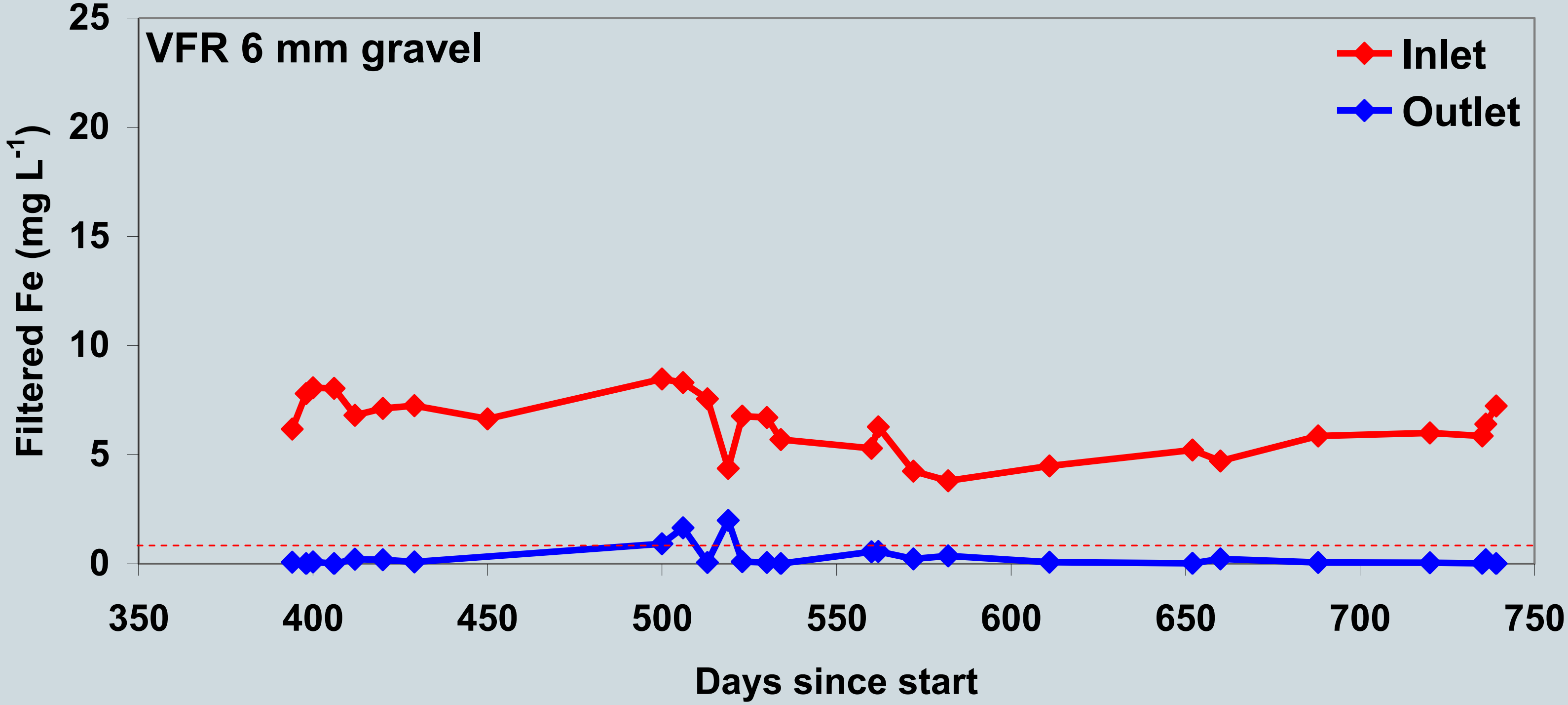

Mean Influent Chemistry

	Mean	n	STDV
pH	6.7	41	0.4
Redox Potential	+ 7.6 mV	39	80.7
Dissolved Oxygen	4.2 mg/L	37	1.1
Temperature	11.8 ^{o}C	40	0.8
Alkalinity (as $CaCO_3$)	220 mg/L	-	-
Sulphate	221 mg/L	-	-
Total Iron	8.4 mg/L	42	2.7
Filtered Iron (0.45µm)	7.3 mg/L	40	0.8

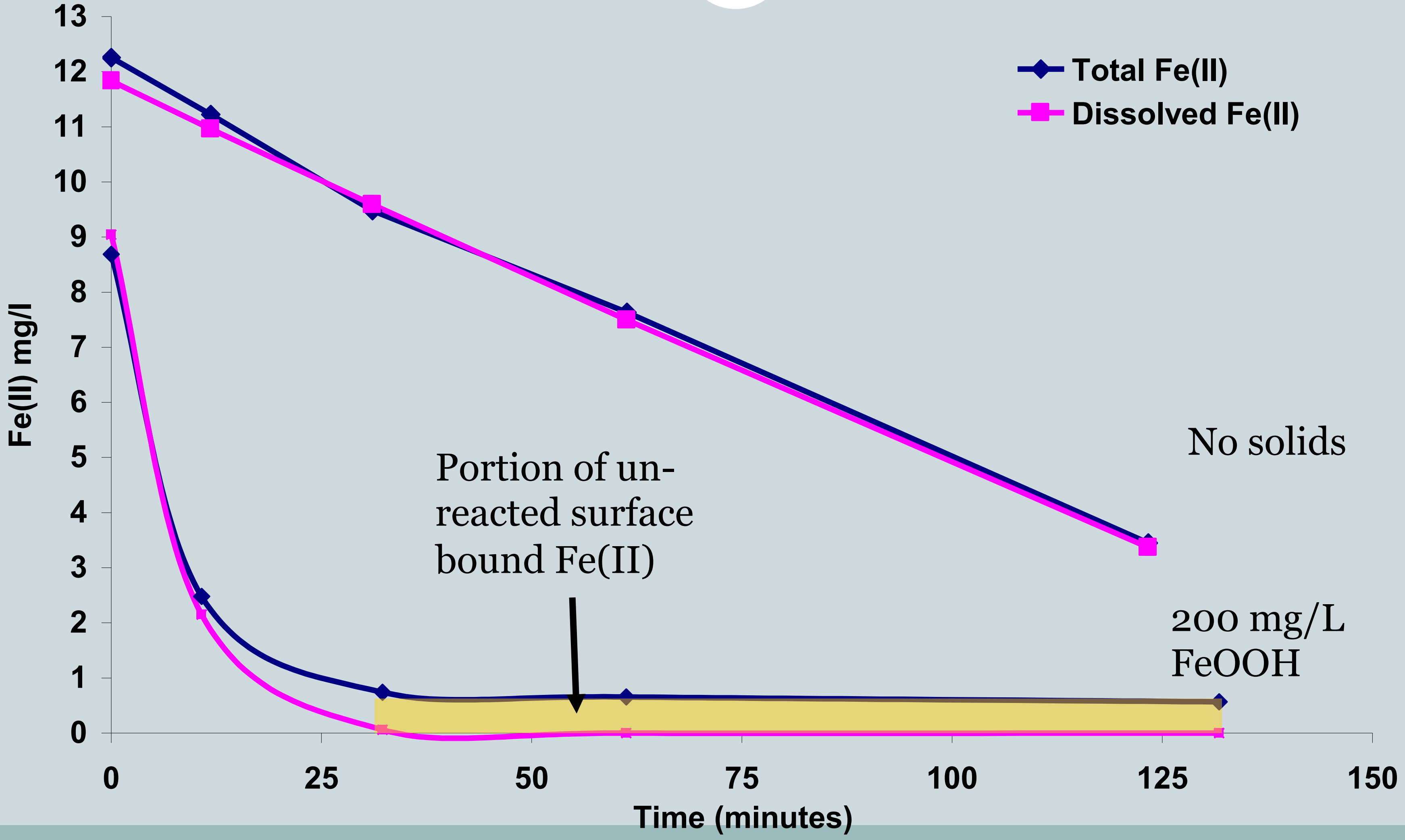
Iron removal mechanisms

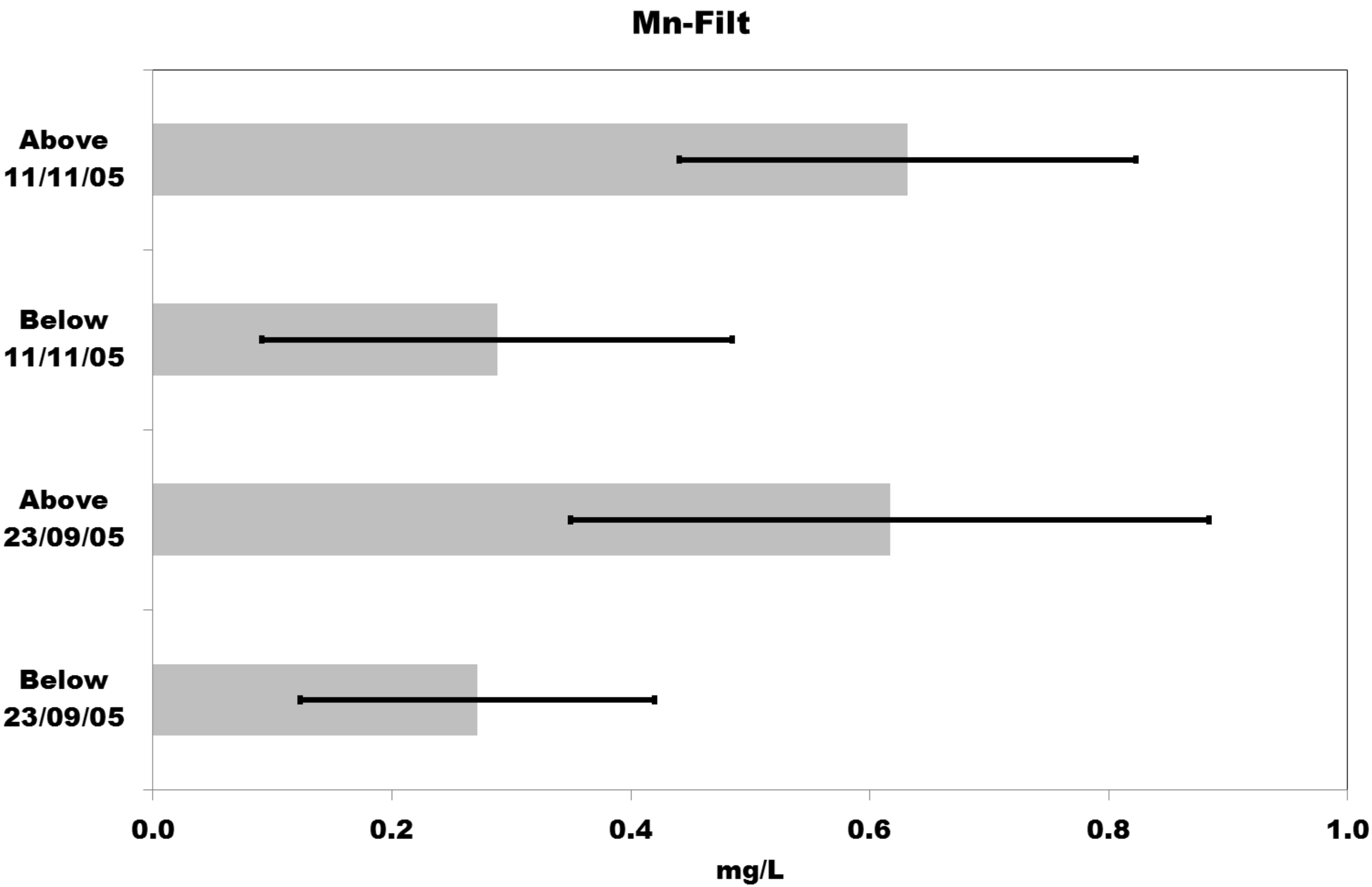


Fe(II) removal

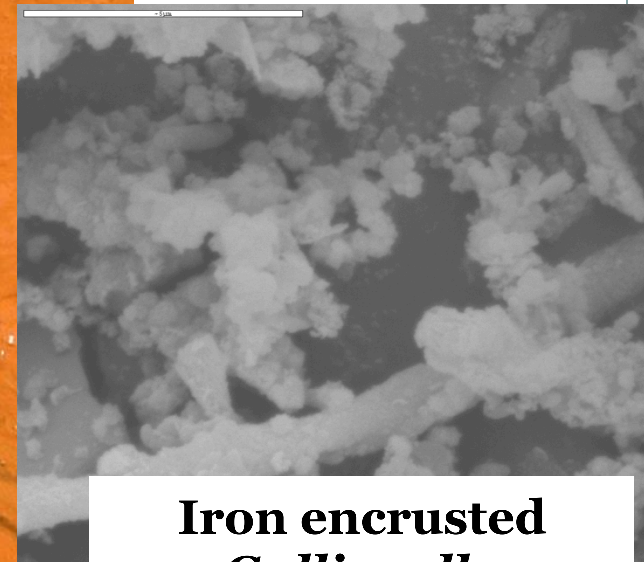


Iron (II) oxidation pH 6

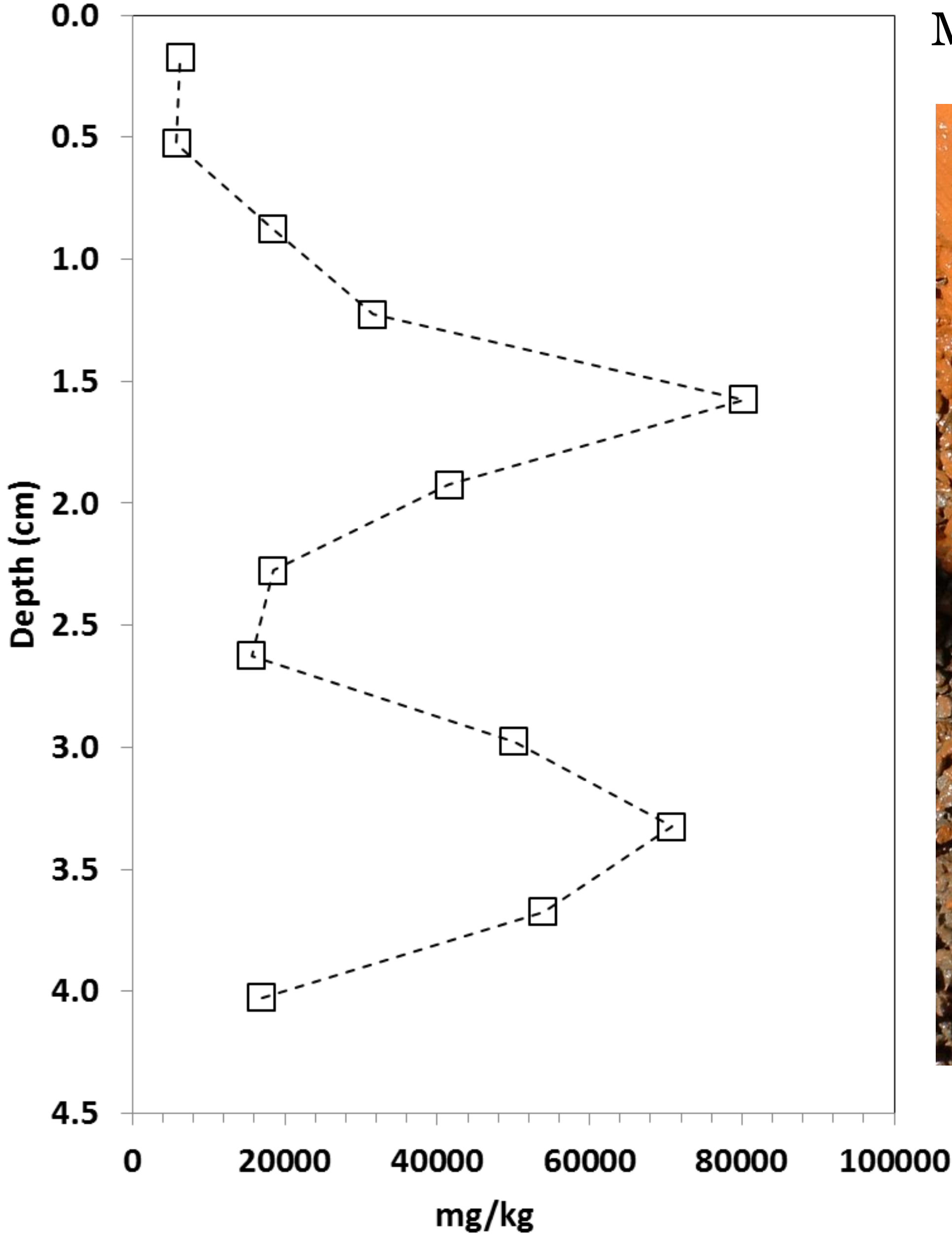




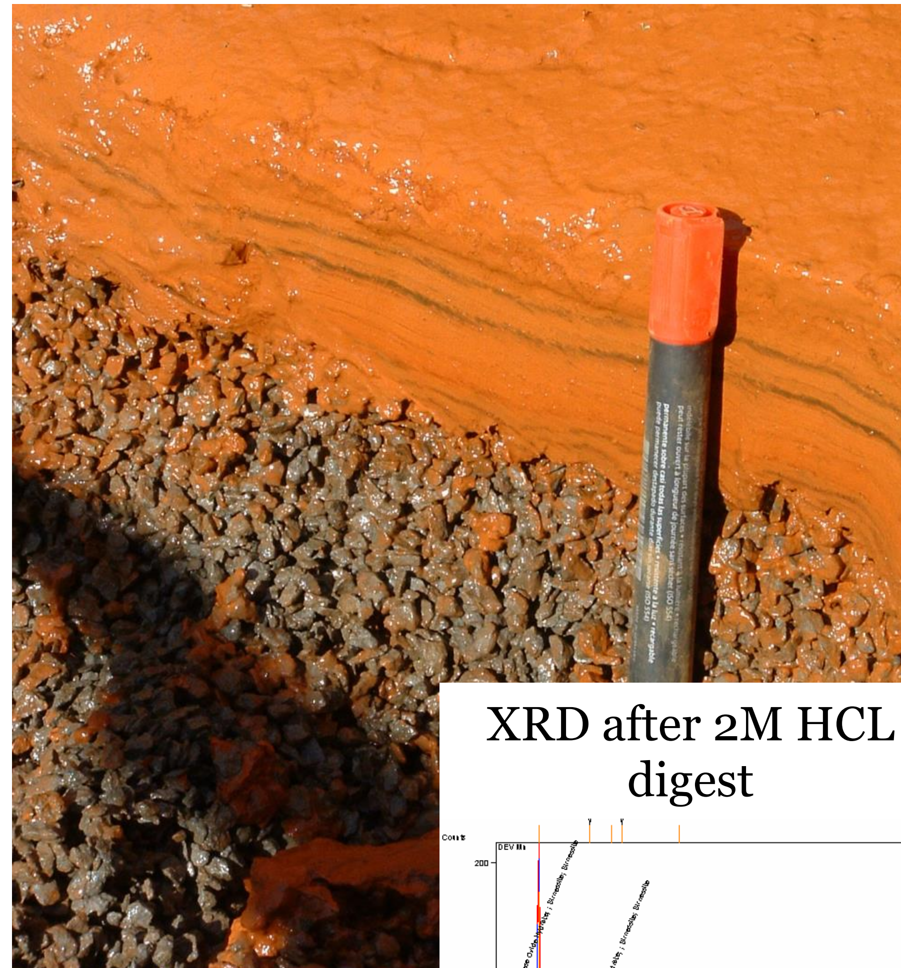
Mn-Filt
Above 11/11/05
Below 11/11/05
Above 23/09/05
Below 23/09/05
0.0
0.2
0.4
0.6
0.8
1.0
mg/L



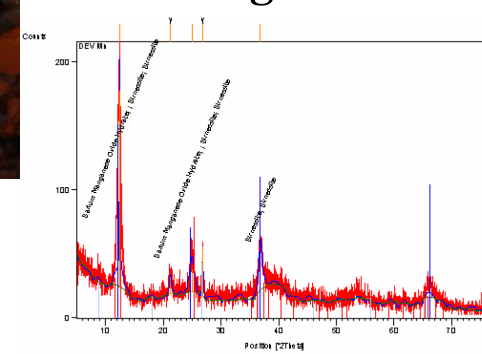
Iron encrusted *Gallionella ferruginea* stalk

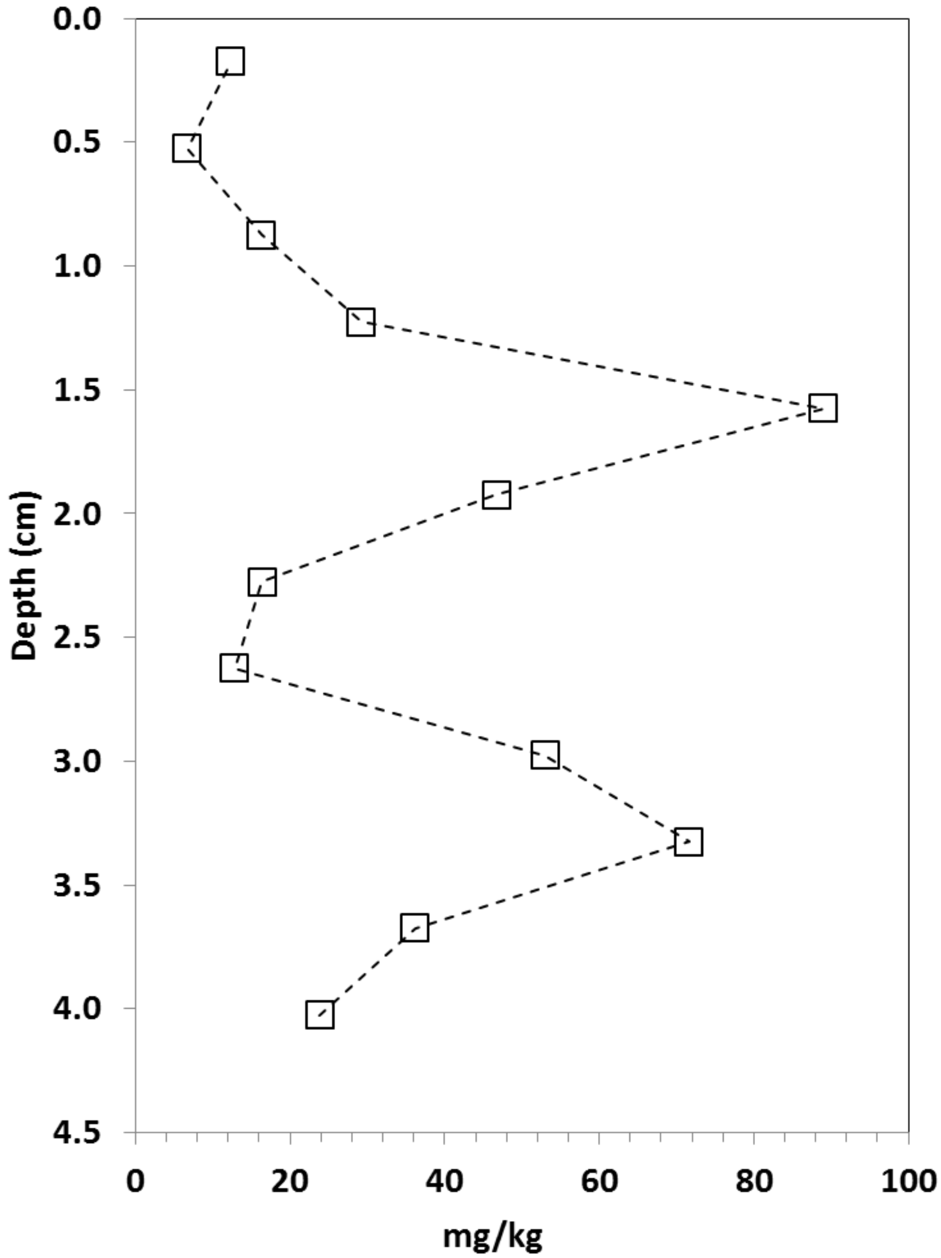


Manganese



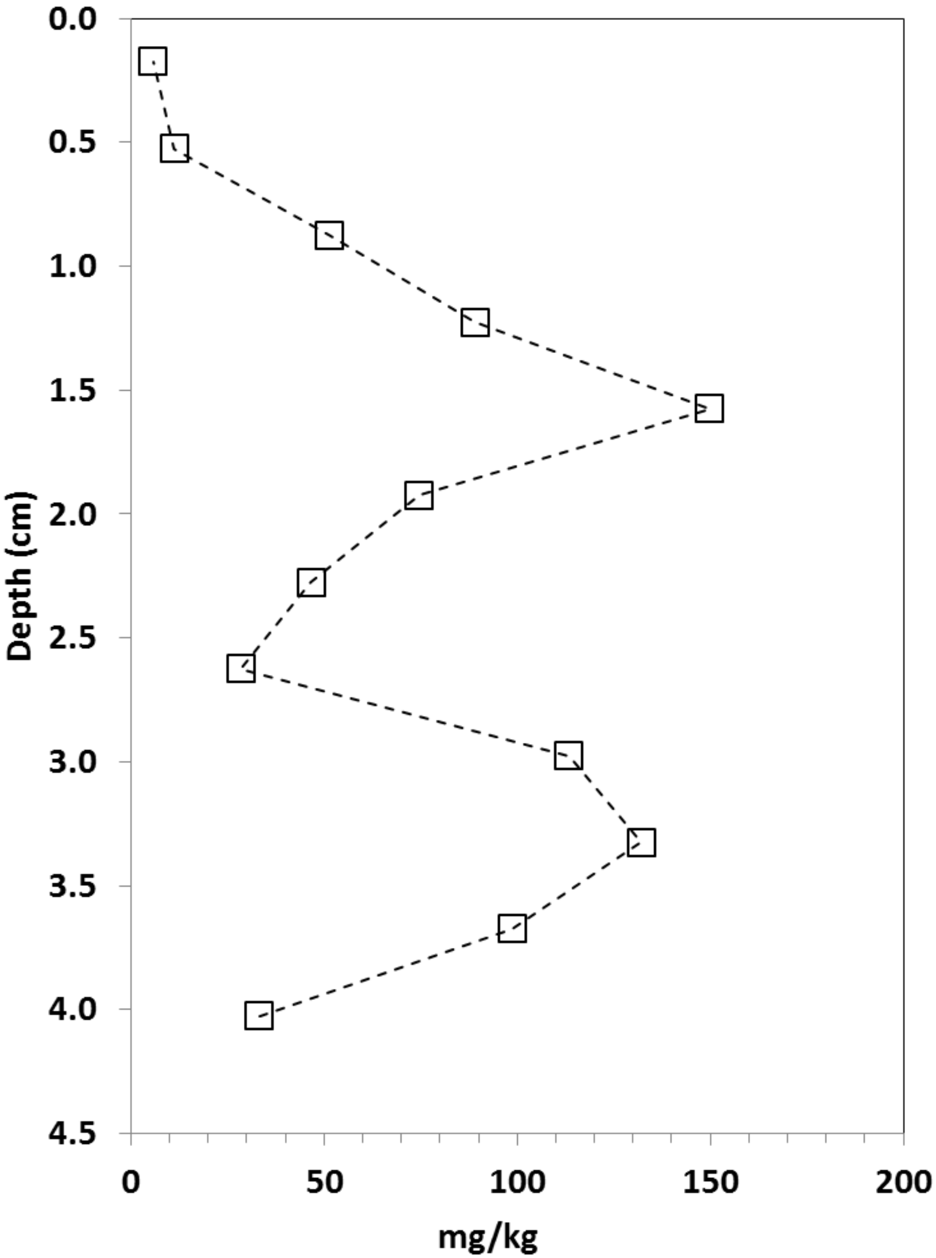
XRD after 2M HCL digest

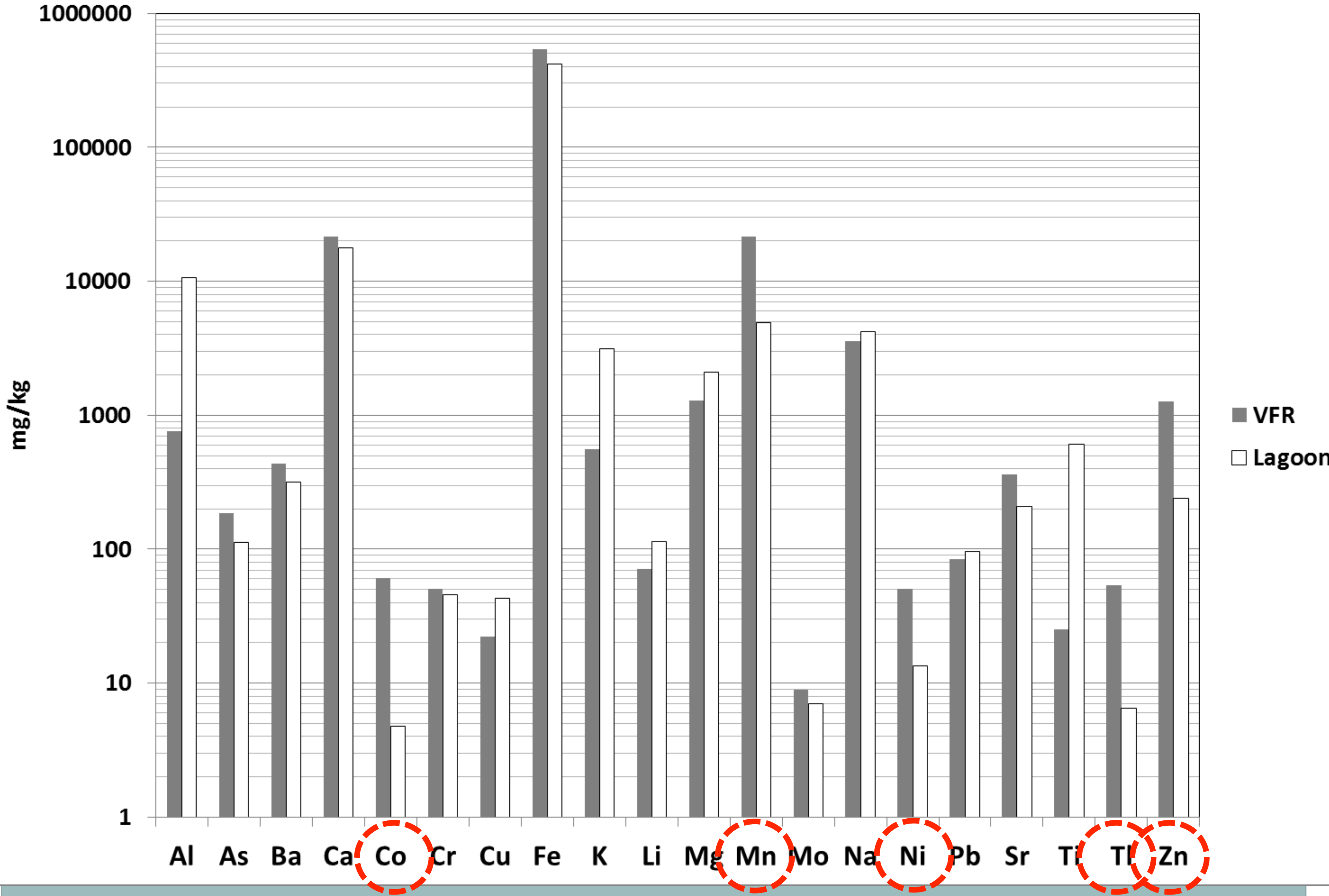




Thallium

Cobalt




1000000
100000
10000
1000
100
10
1
mg/kg
Al
As
Ba
Ca
Co
Cr
Cu
Fe
K
Li
Mg
Mn
Mo
Na
Ni
Pb
Sr
Ti
Tl
Zn
VFR
Lagoon

Summary of circumneutral VFR

- Successful iron removal by (i) aggregation and filtration of particulate iron (ii) Autocatalytic iron oxidation. Iron can be removed from system for recovery/re-use

- Engineering calcs show as a rule of thumb, a quarter the size of conventional passive system for same flow (probably about half the cost).

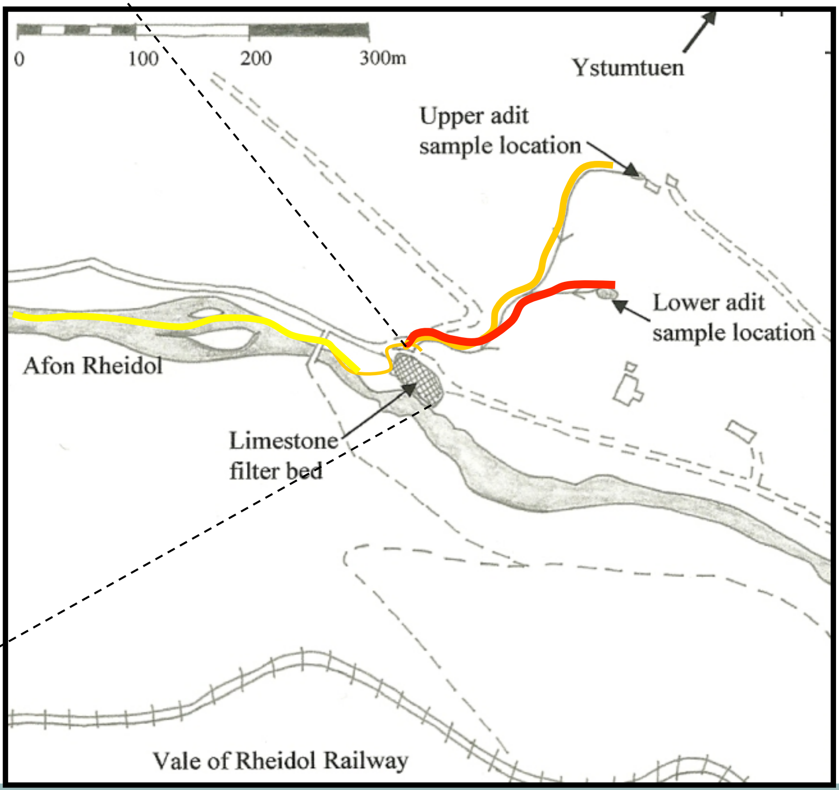
- Microbial analyses indicates very diverse (trapping live and dead microorganisms washing out of the mine)

- Manganese oxidation and removal in 'varve-like' layers.

- Reactive transport calcs show highest rate of Mn (II) in literature k = 164 d^{-1} e.g. compared to 0.07 d^{-1} (Diem and Stumm ,1984)

Will a VFR work at low pH?

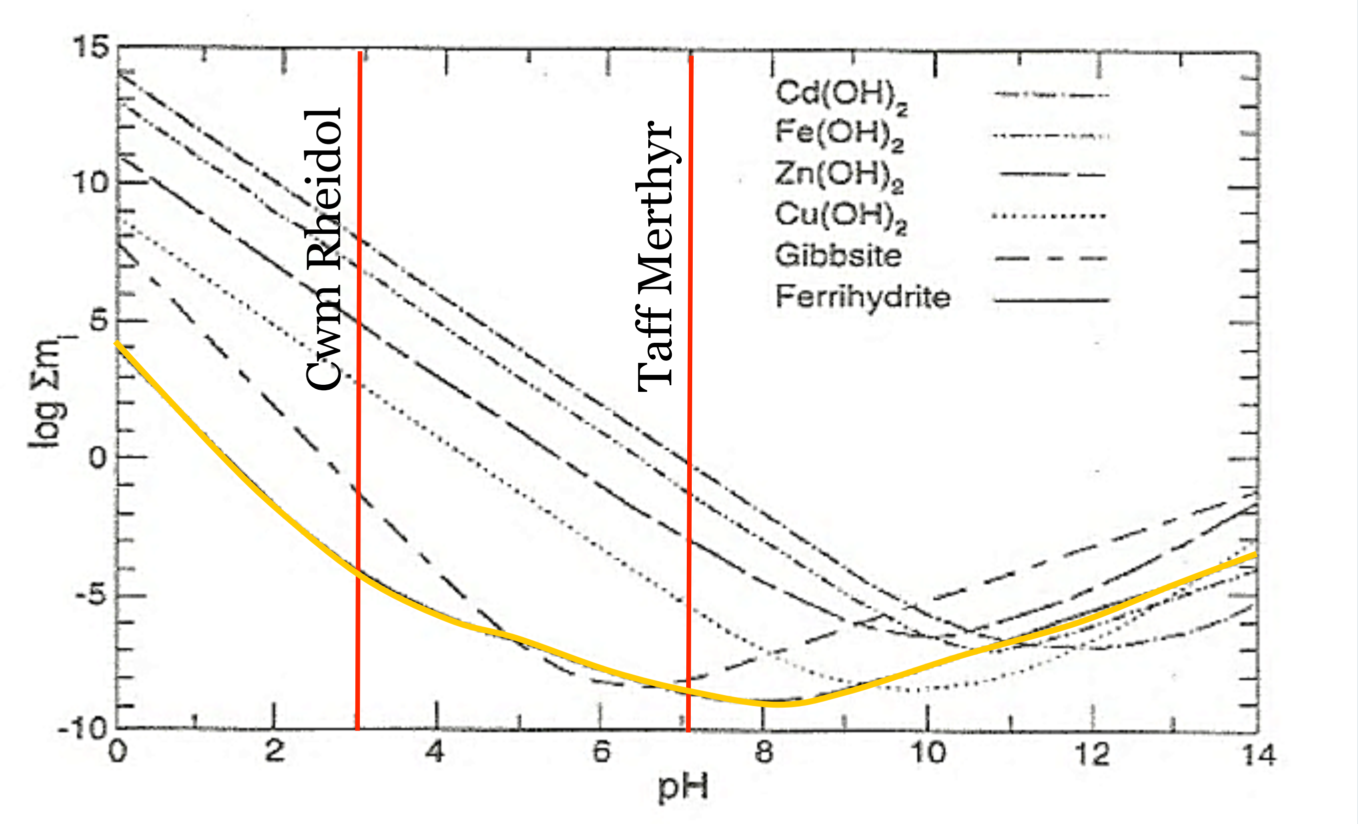
Low pH 2.4 – 3.4
Zn 100 mg/L
High Fe > 100 mg/l



Fe 21.5 mg/L

Filter beds at Cwm Rheidol

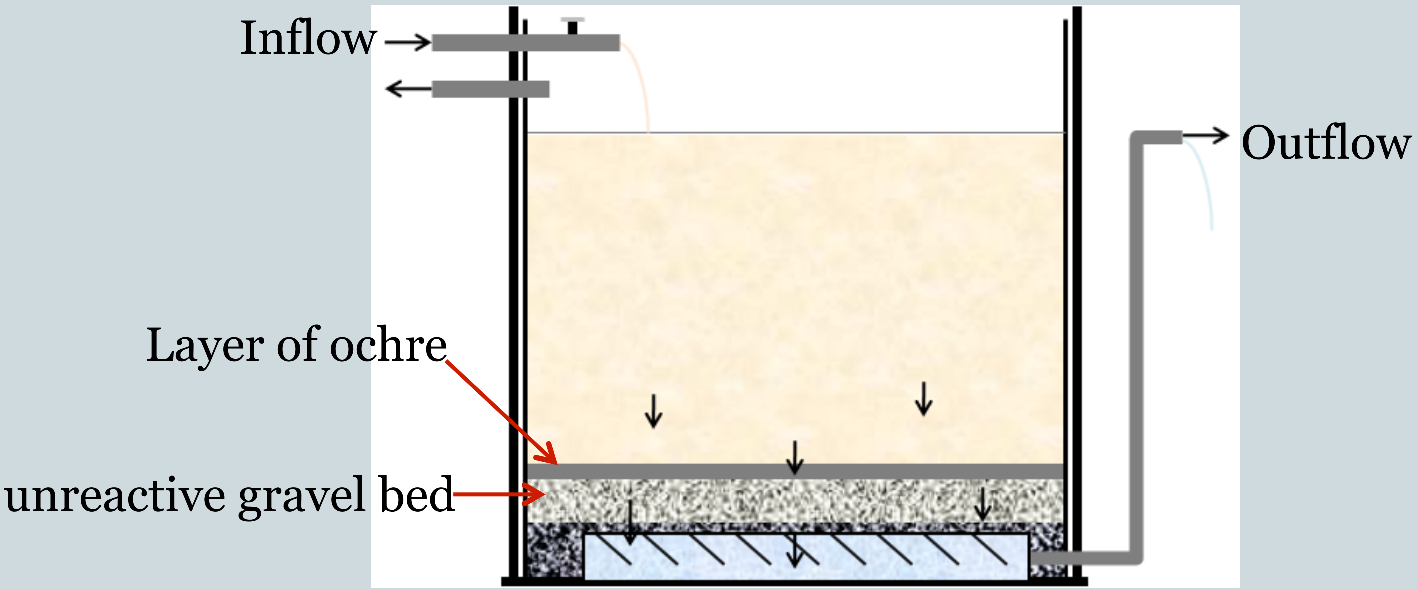
Fe removal at low pH?



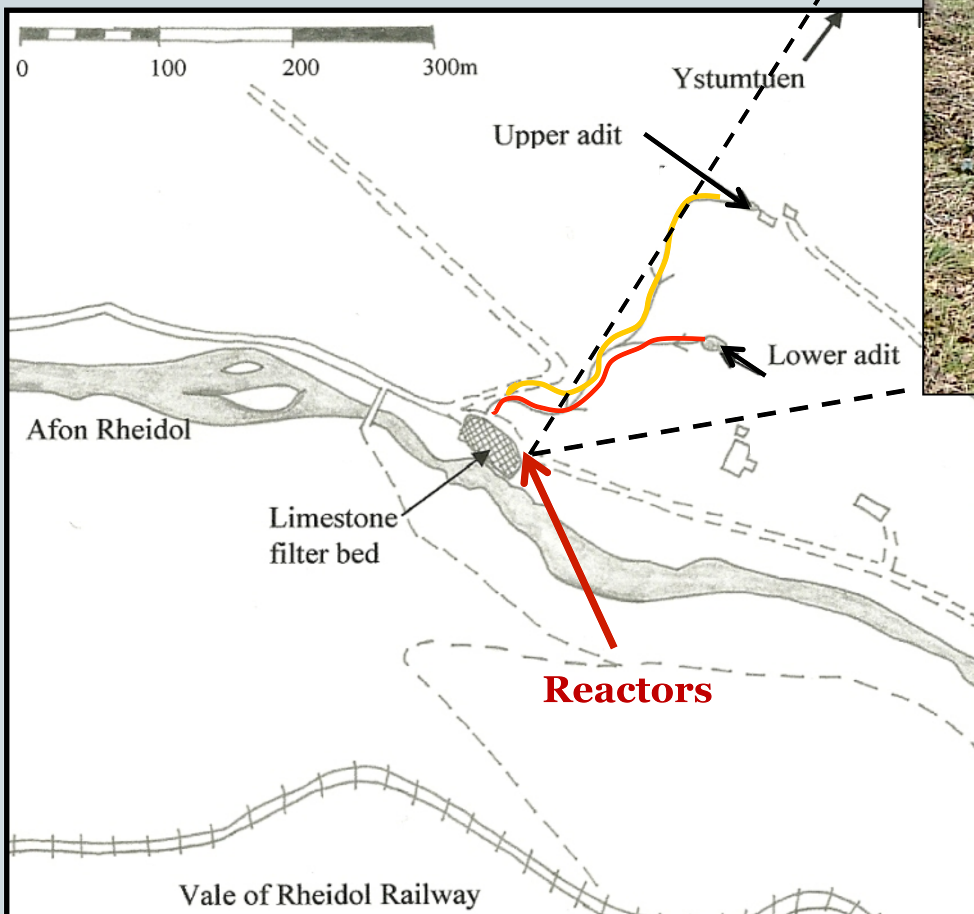
Solubility over the pH range 0 – 14 adapted from Nordstrom & Alpers 1999

Vertical flow reactor

- Gravel bed iron filtration system



Location of VFR



Discharge Chemistry

Water quality data for adit number 9

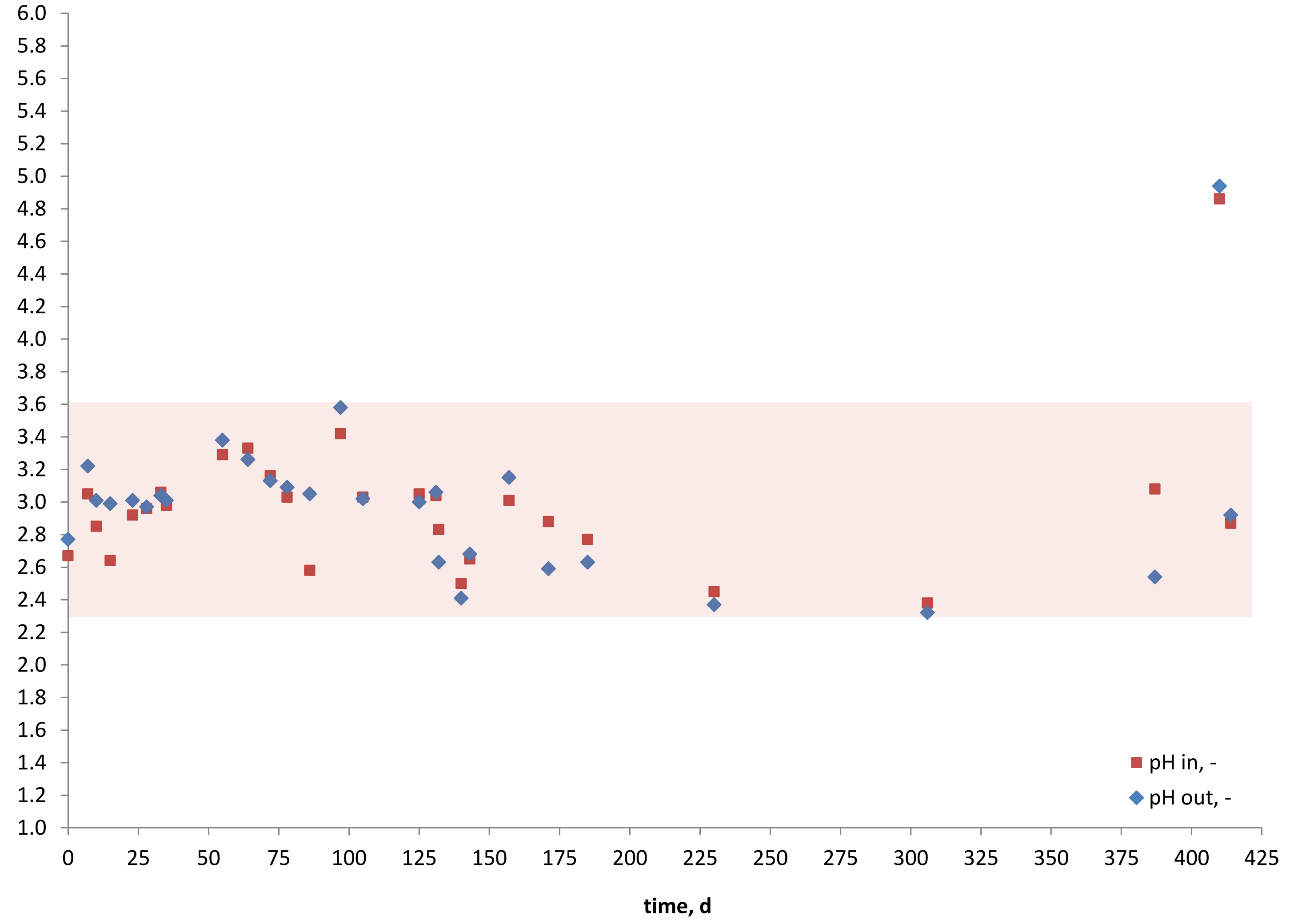
Flow rate	1 L/s
pH	2.9 (std. dev. 0.4)
ORP (Rel.mV)	652
EC (µS/cm)	1544
D.O (mg/L)	8.0
Fe_{total}	100 mg/L
Zn	100 mg/L

Metal removal

mg/L	Fe (tot)	Fe (filtered)	Zn	Cd	Pb	SO_4^{2-}	Cl^-
Inflow	95.9 ±29.7	89.2 ±32.3	100.7 ±21.9	0.14 ±0.09	0.10 ±0.14	1485 ±438	17.1 ±20.0
Outflow	31.4 ±15.6	36.3 ±22.9	99.0 ±21.8	0.13 ±0.03	0.05 ±0.02	1478 ±415	13.8 ±6.5
n	21	27	27	22	25	22	20

Consistently removing approximately 70% of the total Fe

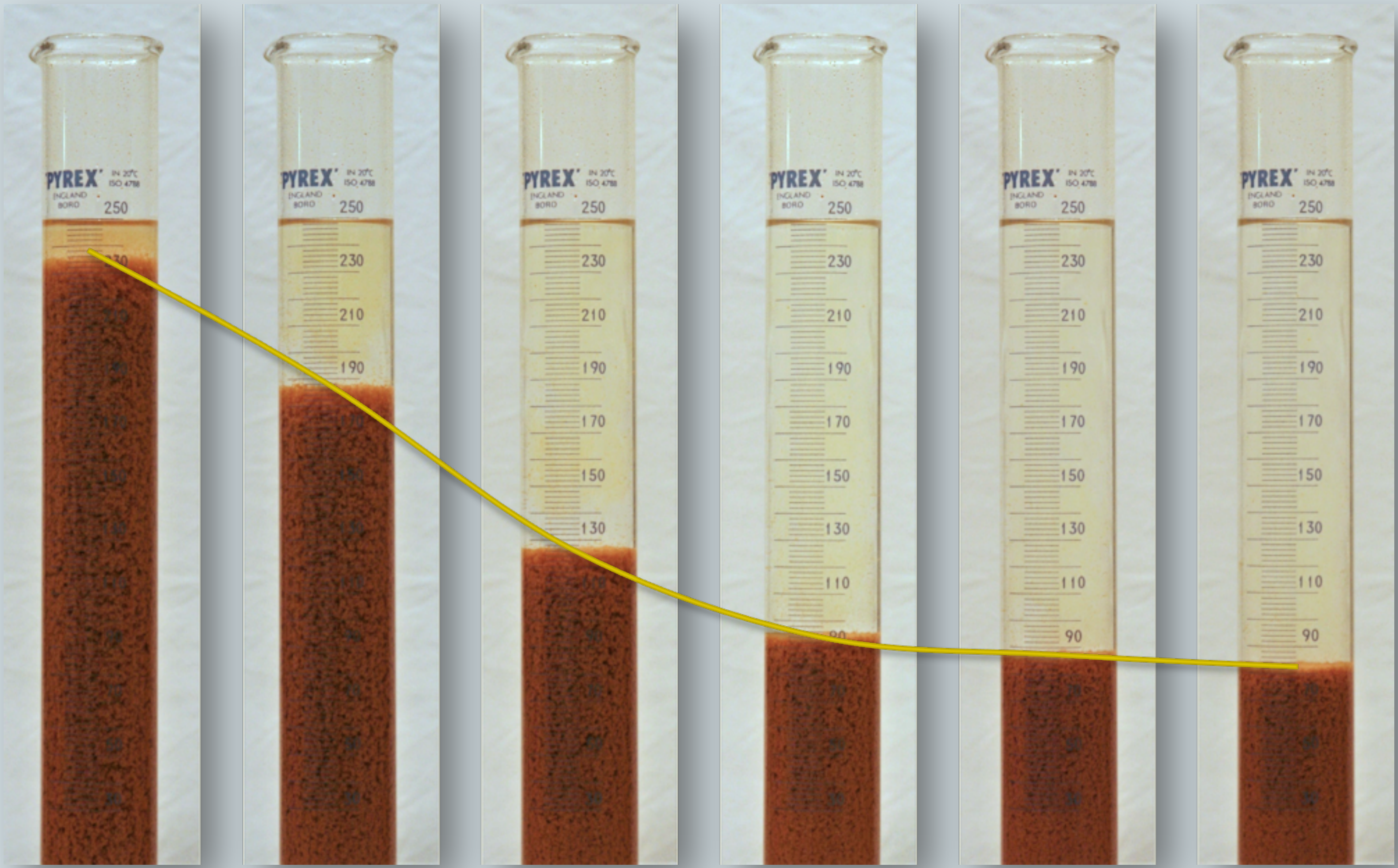
pH


6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0
25
50
75
100
125
150
175
200
225
250
275
300
325
350
375
400
425
time, d
pH in, -
pH out, -

Fe removal in VFR

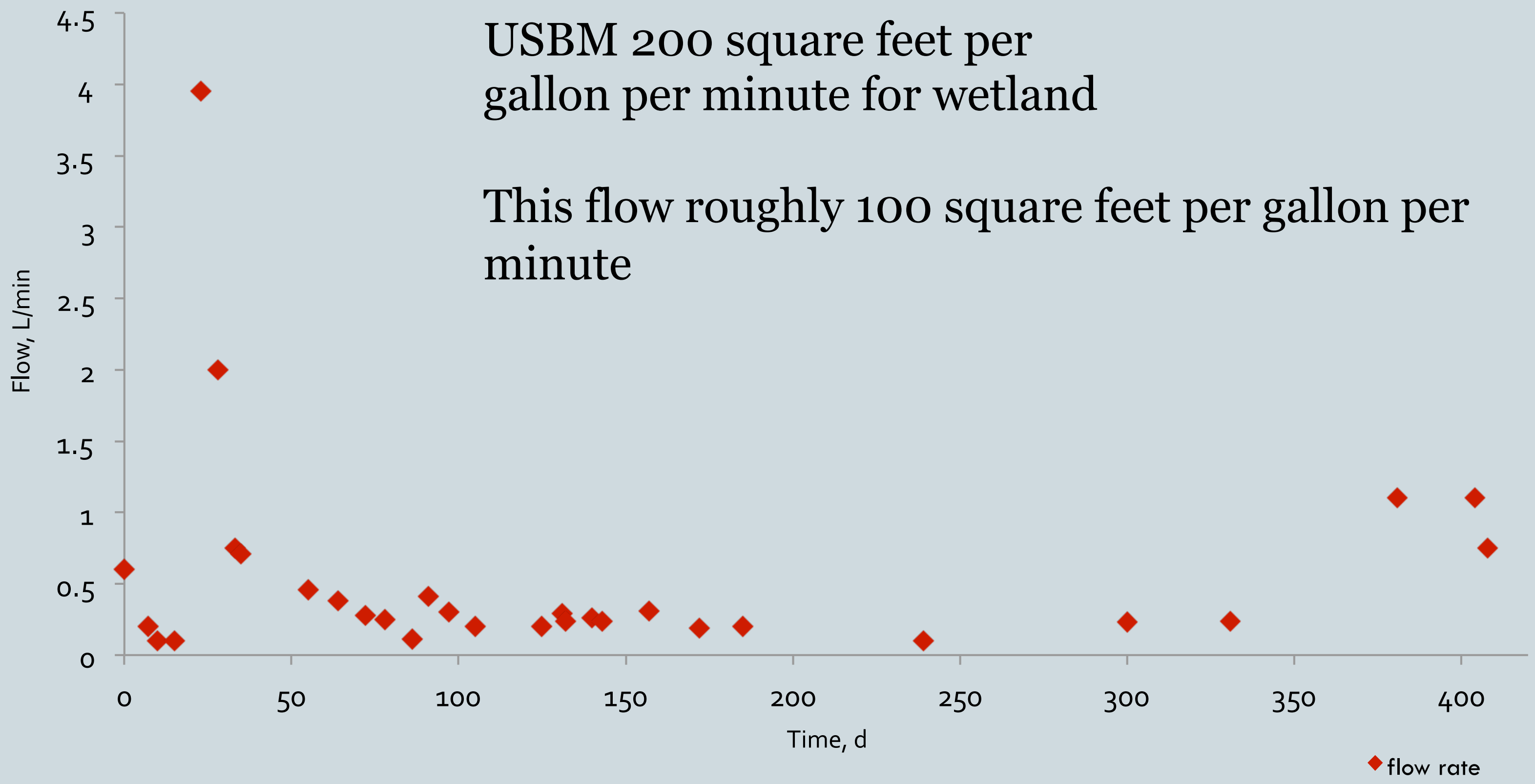
≈ 70% of the total Fe passing a 0.2 µm filter is retained in the tank

Settling properties



15 s 60 s 120 s 180 s 240 s 300 s

Flow rate over time



USBM 200 square feet per gallon per minute for wetland

This flow roughly 100 square feet per gallon per minute

After the initial period of the tank filling, flow rate has remained relatively constant with 20 cm driving head

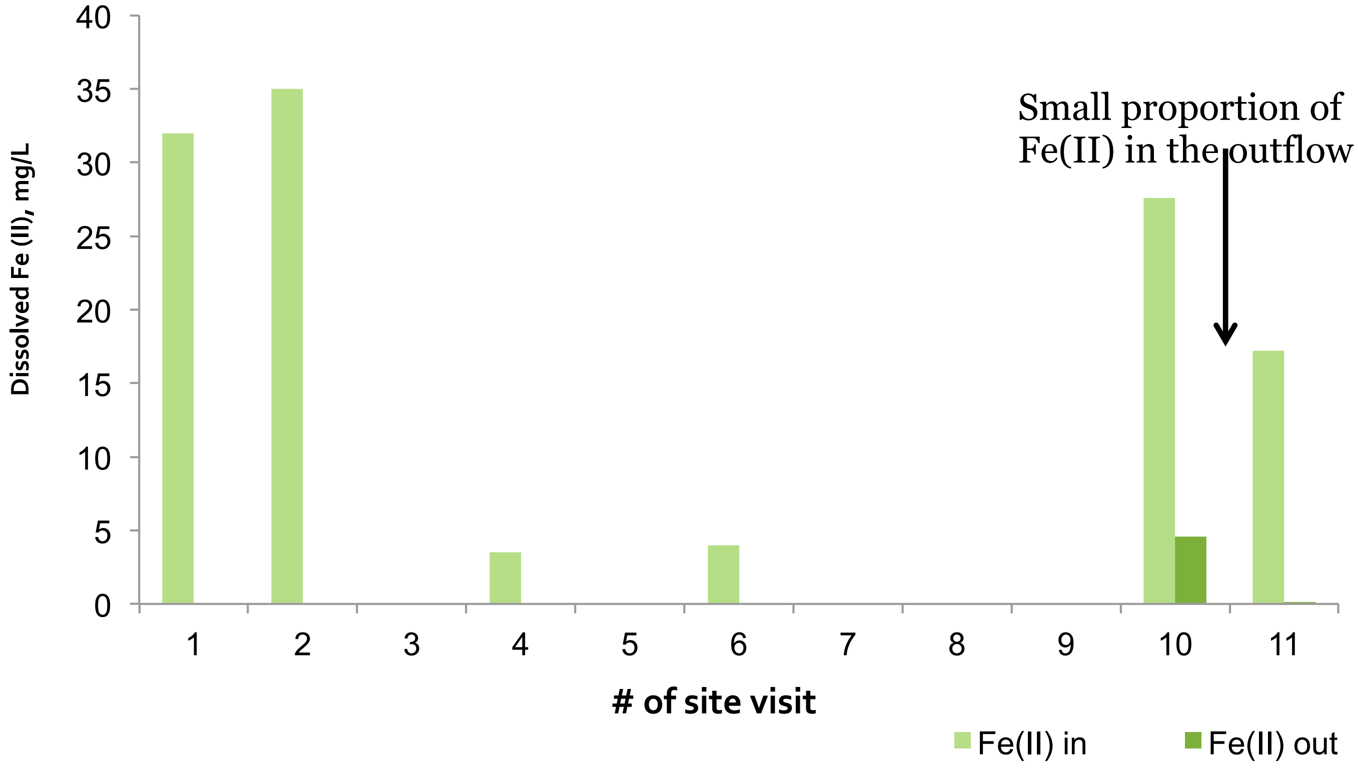
Possible Fe removal mechanisms

Microbial oxidation of Fe(II)

?

?

Evidence for some Fe(II) oxidation



Variable from <5 mg/L to 35 mg/L Fe(II)

Microbial ecology investigation

- Collaboration with Prof Barrie Johnson and Dr Catherine Kay, Bangor University, UK

  - Analysis of water and sludge samples

  - **simple community dominated by the iron-oxidizing β-proteobacterium *Ferrovum myxofaciens***
    - approximately 50 % relative abundance

  - increasingly identified within acidic free-flowing waters and with formation of long gelatinous extracellular polysaccharide (EPS) matrixes (filament)

  - adheres to organic and inorganic materials providing a mechanism of attachment within the flowing stream

  - ensures access to the soluble Fe^{2+} energy source transported by the stream

Stirring experiment done when no Fe(II) present

Raw mine water	Fe-filt (0 hours) (mg/L)	Fe-filt (6 hours) (mg/L)
Still (no ochre)	58	50
Agitated (no ochre)	57	20
Agitated (ochre added)	45	28

Agitation seems to be the common feature, not the addition of sorption material

Possible Fe removal mechanisms

Filtering of colloidal Fe(III) particles	Microbial oxidation Fe(II)	Heterogeneous oxidation of Fe(II)	Sorption of dissolved Fe(III)
Fe conc decrease with agitation (coagulation/ Aggregation)	Fe oxidising bacteria present in the water	Not always Fe(II) present, rate of heterogeneous oxidation is very slow at low pH	Dissolved Fe(III) concentration of treated water does not decrease when solid added
YES	SOME	UNLIKELY	UNLIKELY

What fraction is truly dissolved?

Centrifuging results

				Analyte Concentration (mg/L)				
Sample #	Centrifuge speed (RPM)	Centrifuge time(hrs)	Particle Diameter (nm)	Fe	Ca	Mg	Al	Zn
Raw Mine Water	-	-	-	99.57	59.47	39.70	27.66	81.63
0	-	-	-	98.24	59.15	39.25	27.84	82.81
1	300	1	683	96.55	63.25	41.39	29.29	84.94
2	500	1	417	92.75	62.06	40.22	28.39	83.73
3	700	1	293	82.05	62.31	40.58	29.18	85.02
4	1000	1	207	91.41	60.18	40.13	28.19	82.94
5	2000	1	101	89.00	61.29	40.21	28.52	84.05
6	4000	1	50	85.66	61.32	40.87	29.24	83.70
7	5000	1	39	84.45	72.66	41.44	28.88	87.08
8	3500	2	35	86.93	61.21	40.87	29.10	83.09

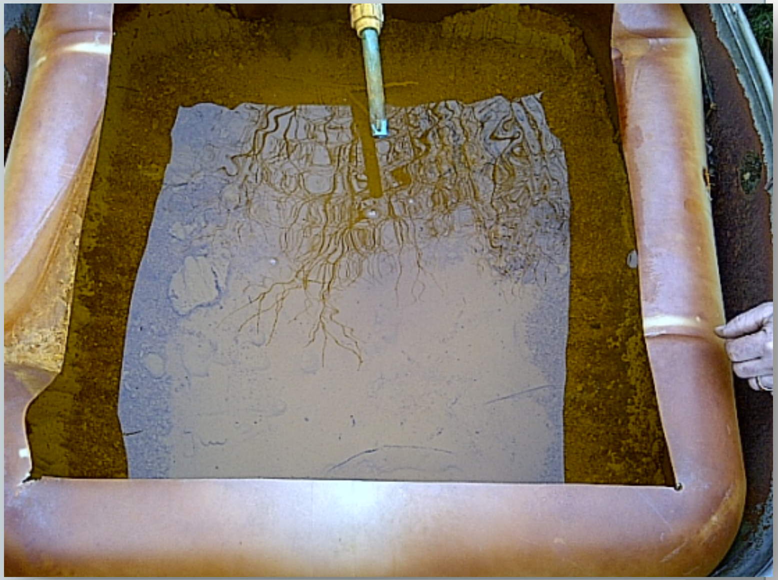
The removal mechanism is…

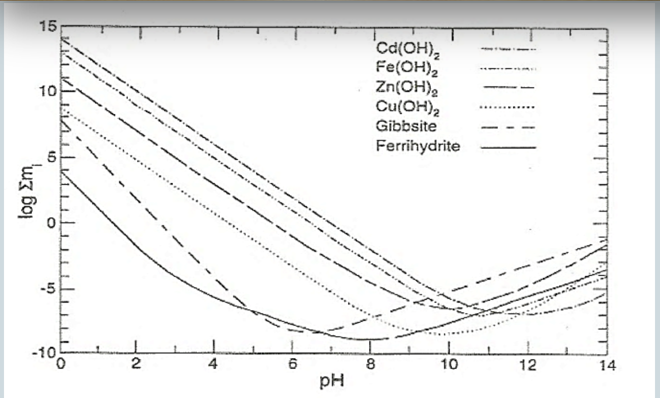
[1] Aggregation of nanoparticulate iron oxides

"Fe(III) phases which form from solution begin as small clusters of octahedral Fe (O, OH, OH2)6 units that evolve into larger polymeric units with time, eventually reaching colloidal sizes (Combes et al., 1989)."

[2] Kinetically constrained iron precipitation
…what we may be seeing is kinetics, the slow hydrolysis of Fe(III)

Perhaps a continuum of the same process?





Summary of VFR pilot studies

Photo: Christian Wolkersdorfer

The VFR is an effective low footprint 'filter' for removal of Fe at low and circumneutral pH. Iron is removed by a combination of physical and biogeochemical mechanisms.

Other sites will be tested…