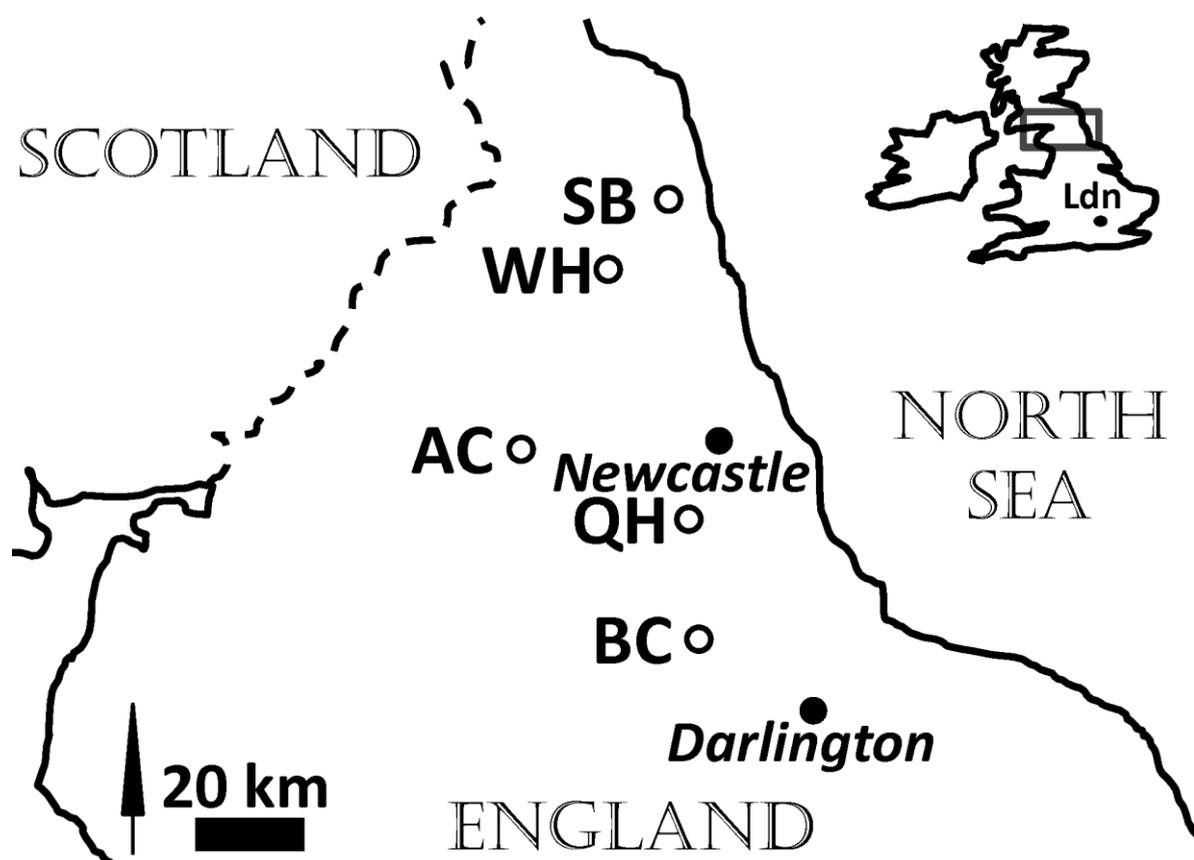## Supplement 1

Location of mine water monitoring sites in NE England; AC = Acomb, BC = Bowden Close, QH = Quaking Houses, SB = Shilbottle, WH = Whittle
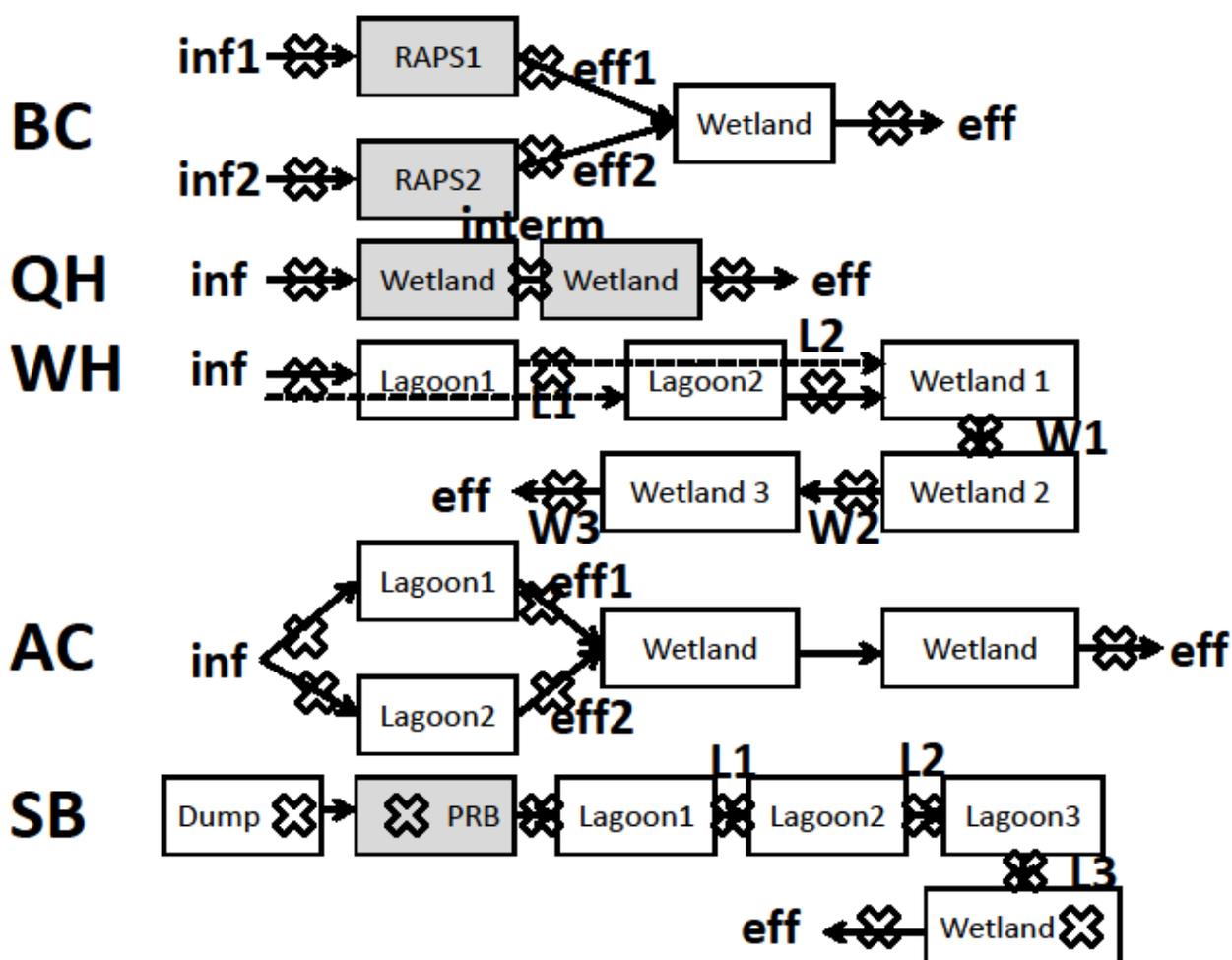
Supplement 2

Physicochemical parameters in mine waters and effluents and percentage iron retention rates in the treatment systems

Site (% Fe retention)	Parameter	Mine water	Effluent
Acomb (60-90)	pH	6.2-6.9	6.5-7.6
	Eh	300-700	490-690
	Alk	190-250	170-260
Bowden Close (9-100)	pH	3.2-6.8	5.9-7.5
	Eh	350-840	360-560
	Alk	0-75	20-190
Quaking Houses (6-47)	pH	6.0-7.0	6.3-7.3
	Eh	340-570	320-470
	Alk	34-100	70-105
Shilbottle (15-97*)	pH	3.1-7.4	3.0-6.2
	Eh	350-900	450-900
	Alk	0-920	0-25
Whittle (87-97)	pH	6.7-6.9	7.7-8.1
	Eh	280-450	350-400
	Alk	470-510	250-450

Minimum - maximum; Eh in mV, Alk = alkalinity in mg L^{-1} $CaCO_3$ eq, *only U1 (a piezometer located in the Shilbottle waste rock dump) iron concentrations considered for the calculation of percentage iron retention

Supplement 3

Oxidative (white background) and reductive (grey backgrounds) passive treatment ponds monitored between 2006 and 2007; Bowden Close (BC, RAPS: Reducing and Alkalinity Producing Systems, sampling points (SP, marked with a cross): inf1: mine water from underground coal mine, inf2: mine water from waste rock dump, eff1,2: effluent of RAPS1,2, eff: final effluent); Quaking Houses (QH, SP: inf: mine water, interm: intermediate sampling point between the subsurface flow wetlands); Whittle (WH, SP: inf: mine water sampled on the aeration cascade, L1,2: effluent of settling lagoons 1,2: effluent of settling lagoon 2, W1,2,3: effluents of aerobic reed beds 1,2,3); Acomb (AC, oxidation of mine water by H_2O_2 dosing, SP: inf: mine water, eff 1,2: effluents of aerobic reed beds 1,2); Shilbottle (SB, mine water sampled from boreholes located in the waste rock dump, SP: in total seven bore holes located in the waste rock dump, four boreholes located in the permeable reactive barrier (PRB), L1,2,3: effluents of setting lagoons 1,2 and 3, W: sampling point within the aerobic wetland)

Supplement 4

Electrochemical methods applied for iron speciation. Information presented in more detail in: Mudashiru, L.K., Aplin, A.C. and Horrocks, B.R., 2011 Voltammetric methods for the speciation of dissolved iron and determination of Fe-containing nanoparticles in mine-water discharge. Analytical Methods 3, 927-936.

In brief, we applied i) differential pulse voltammetry (DPV, EG & G Princeton Applied Research Potentiostat / Galvanostat Model 263A, detection limit $\approx 10^{-8}$ M, pulse height = 75 mV, pulse width = 50 ms, step scan = 2 mV, scan rate = 10 mV s^{-1}, range: 0.8—1.2 V) and ii) cyclic voltammetry (CV, AEW2-10 by Sycopel Scientific: scan rate = 100 mV s^{-1} for microelectrodes (ME)). CV and DPV analyses were run in standard glass three-electrode cells containing 10 mL sample (2 mm diameter Au disc working electrode, Pt counter electrode, saturated calomel reference electrode, Sycopel Scientific). Each sample was run in triplicate. Electrodes were cleaned sequentially by alumina polishing, de-ionized water, alcohol (99%) and sonication (2 min). Before each measurement and again after six voltammetric runs, electrodes were conditioned for two minutes. The electrochemical cell was bubbled with nitrogen to purge oxygen from the sample. An ultramicroelectrode (UME, 50 μm diameter Pt disc, 10 mV s^{-1} scan rate) was used for steady-state Voltammetry using the same counter and reference electrodes as for CV and DPV (Mudashiru et al., 2011) for the analysis of iron redox species. Anodic and cathodic diffusion limited currents that are proportional to the respective concentrations were measured to discriminate iron redox states in the dissolved phase. The equipment was calibrated using reagent grade 0.1 M KCl and 0.1 M Na$_2$SO$_4$ as background electrolytes and reagent grade Fe salts. Results obtained by DPV were compared to ICP-OES. Results differed within 10% and correlation coefficients (R^2) ranged between 0.92-0.94 with a mean percentage deviation of -2.6-0.6%, excluding outliers. Best agreement between electrochemical and spectroscopic methods was achieved at iron concentrations in the range of 10-100 mg L^{-1} (detection limit ≤5 mg L^{-1} (Mudashiru et al., 2011)).
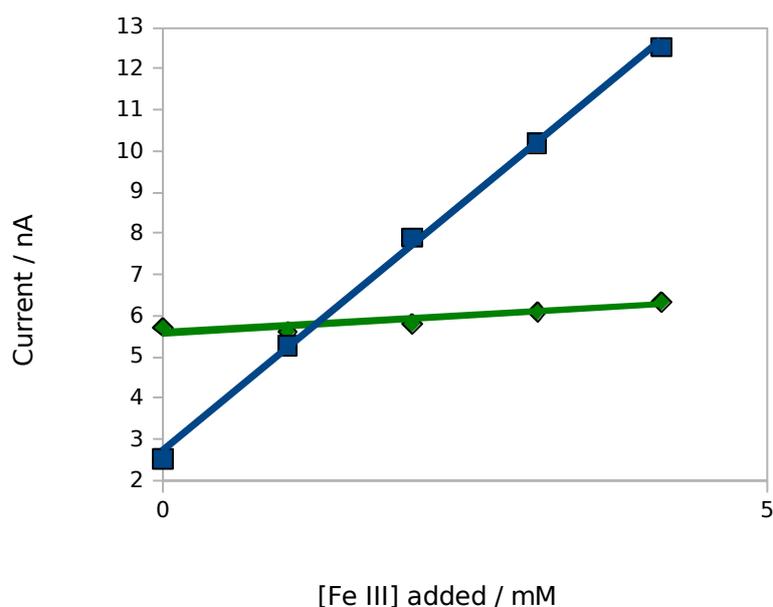

[Fe III] added / mM

Figure 1. Standard addition experiment to determine Fe (III) and Fe(II) in a minewater sample from a settlement lagoon at Shilbottle. The blue squares are the cathodic diffusion-limited quasi-steady state currents (proportional to [Fe(III)]) and the green diamonds are the corresponding anodic limiting currents (proportional to [Fe(II)]). The graph these currents against the concentration of $Fe_2(SO_4)_3$(aq) injected by micropipette from a stock solution of concentration 0.103 M. Extrapolation of the linear plot gives [Fe(III)] = 1.0 $\pm$ 0.08 mM and the assumption of equal diffusion coefficients plus the anodic limiting current gives [Fe(II)] = 2.3 $\pm$ 0.18 mM in this particular example. The uncertainties are standard errors from the linear regression analysis.
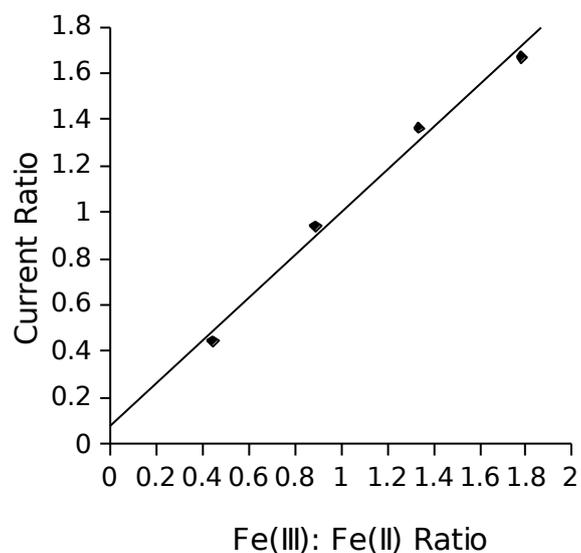

Figure 2. Ratio of cathodic and anodic diffusion-limited currents versus the ratio of Fe(III):Fe(II) in the sample from Shilbottle above containing 1.0 mM Fe(III) and 2.3 mM Fe(II). The ratio Fe(III):Fe(II) was controlled by standard addition of $Fe_2(SO_4)_3$(aq). The slope of the best fit line is 0.92 $\pm$ 0.07; perfect agreement corresponds to a slope of 1.

References

Mudashiru, L.K., Aplin, A.C. and Horrocks, B.R., 2011 Voltammetric methods for the speciation of dissolved iron and determination of Fe-containing nanoparticles in mine-water discharge. Analytical Methods 3, 927-936.
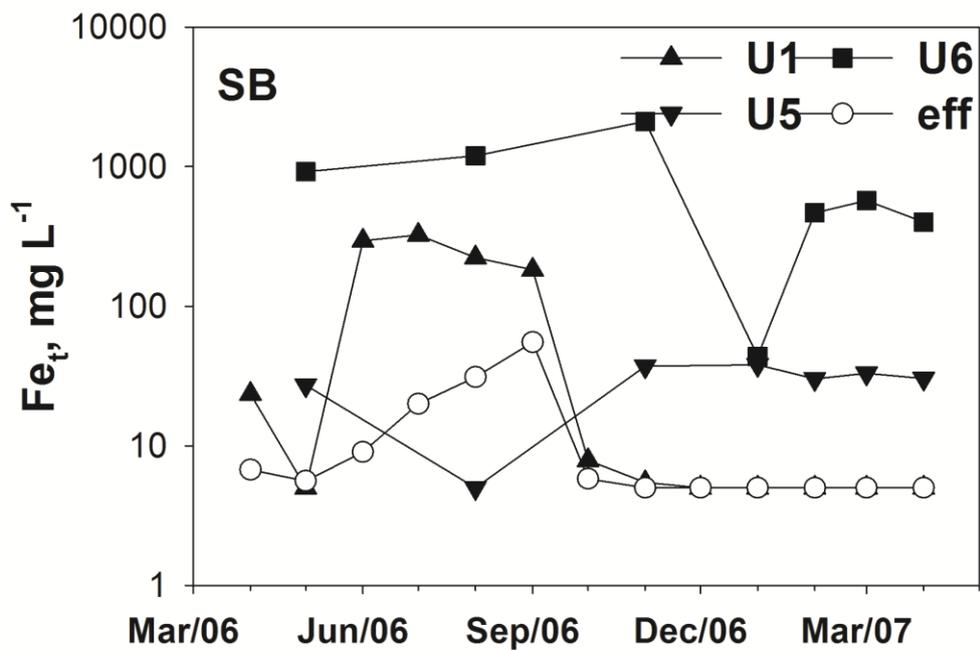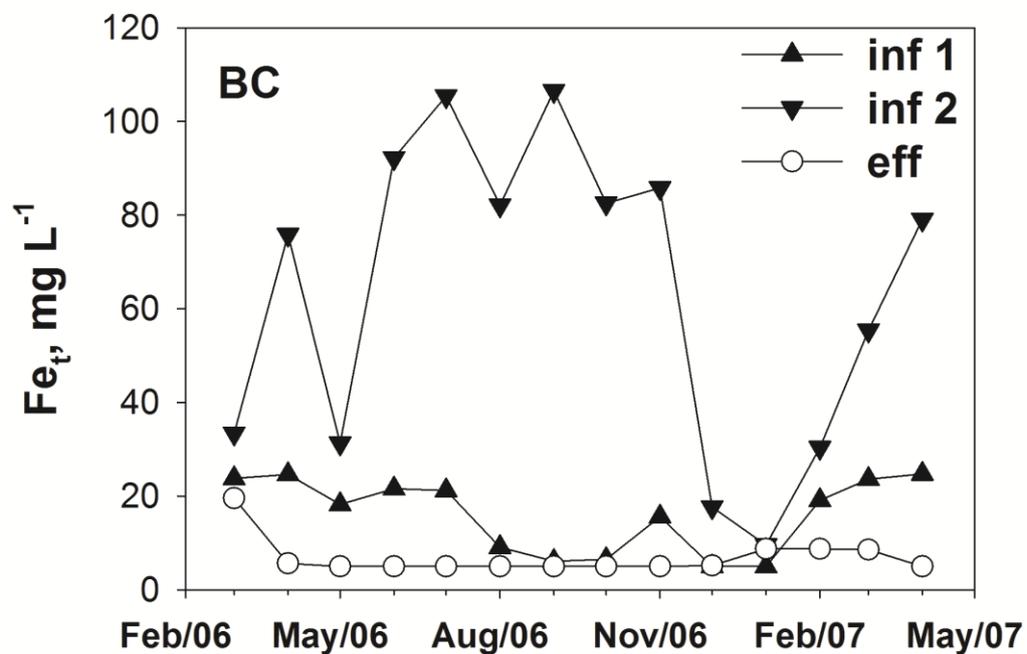
Supplement 5

Total iron concentrations measured in mine waters and final effluents of five passive treatment systems; thick solid line: average; solid line: median; limitation of boxes: 25 and 75% quartiles; whiskers: 5 and 95% quartiles; numbers above box plots: number of samples; inf: mine waters; eff: final effluents of passive treatment systems; U: water collected from boreholes within the Shilbottle waste rock dump; AC: Acomb, BC: Bowden Close, QH: Quaking Houses, SB: Shilbottle, WH: Whittle
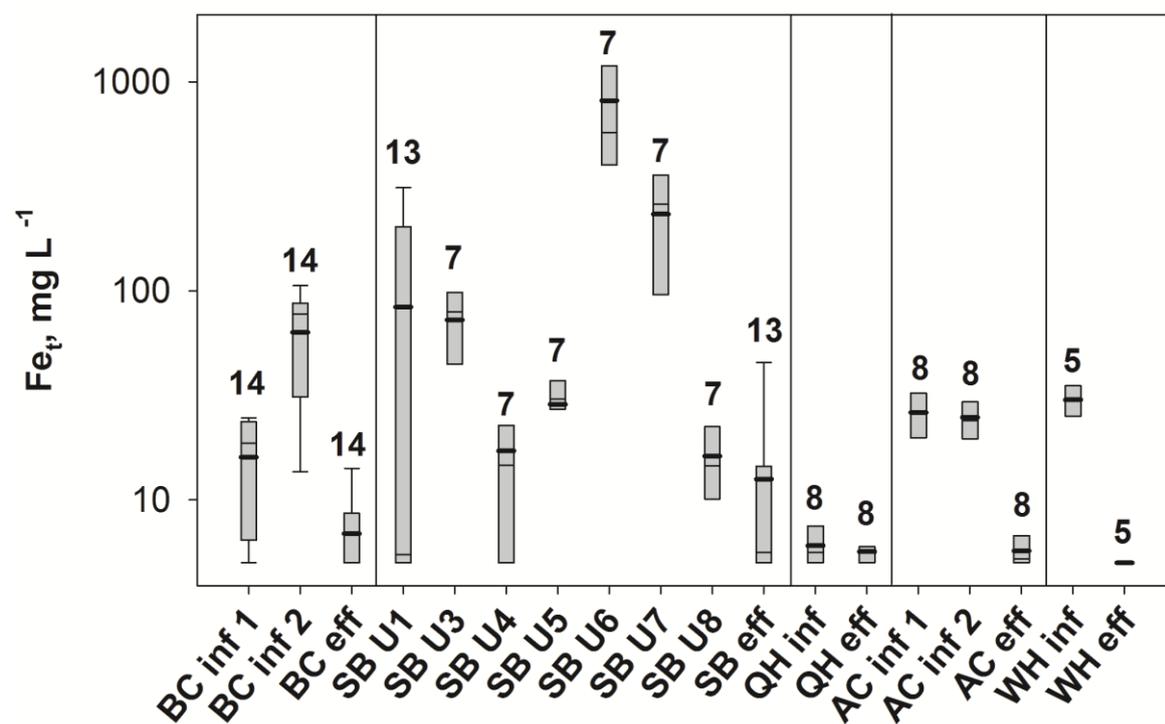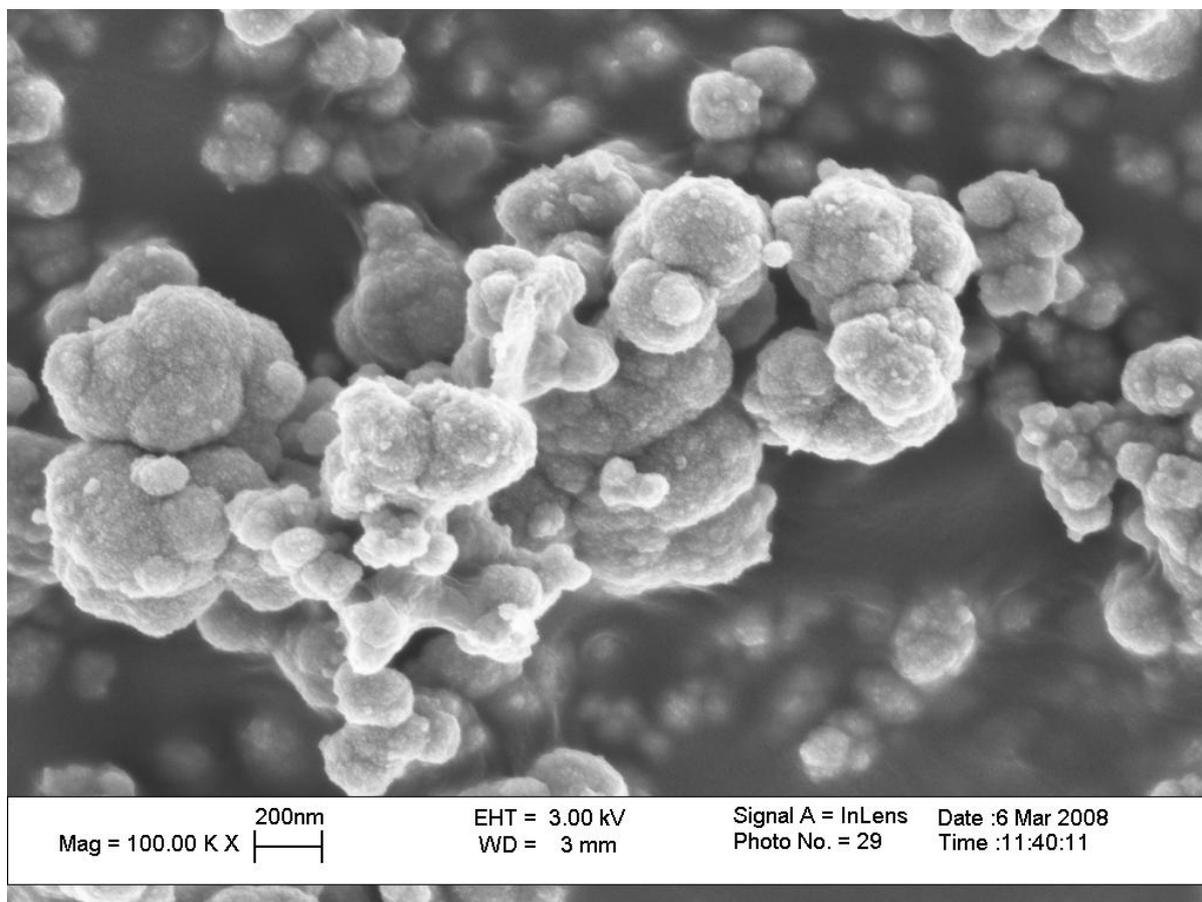
Supplement 6

Seasonal variations of total iron concentrations in influents of Bowden Close (BC) and Shilbottle (SB) and in effluent of both treatment schemes
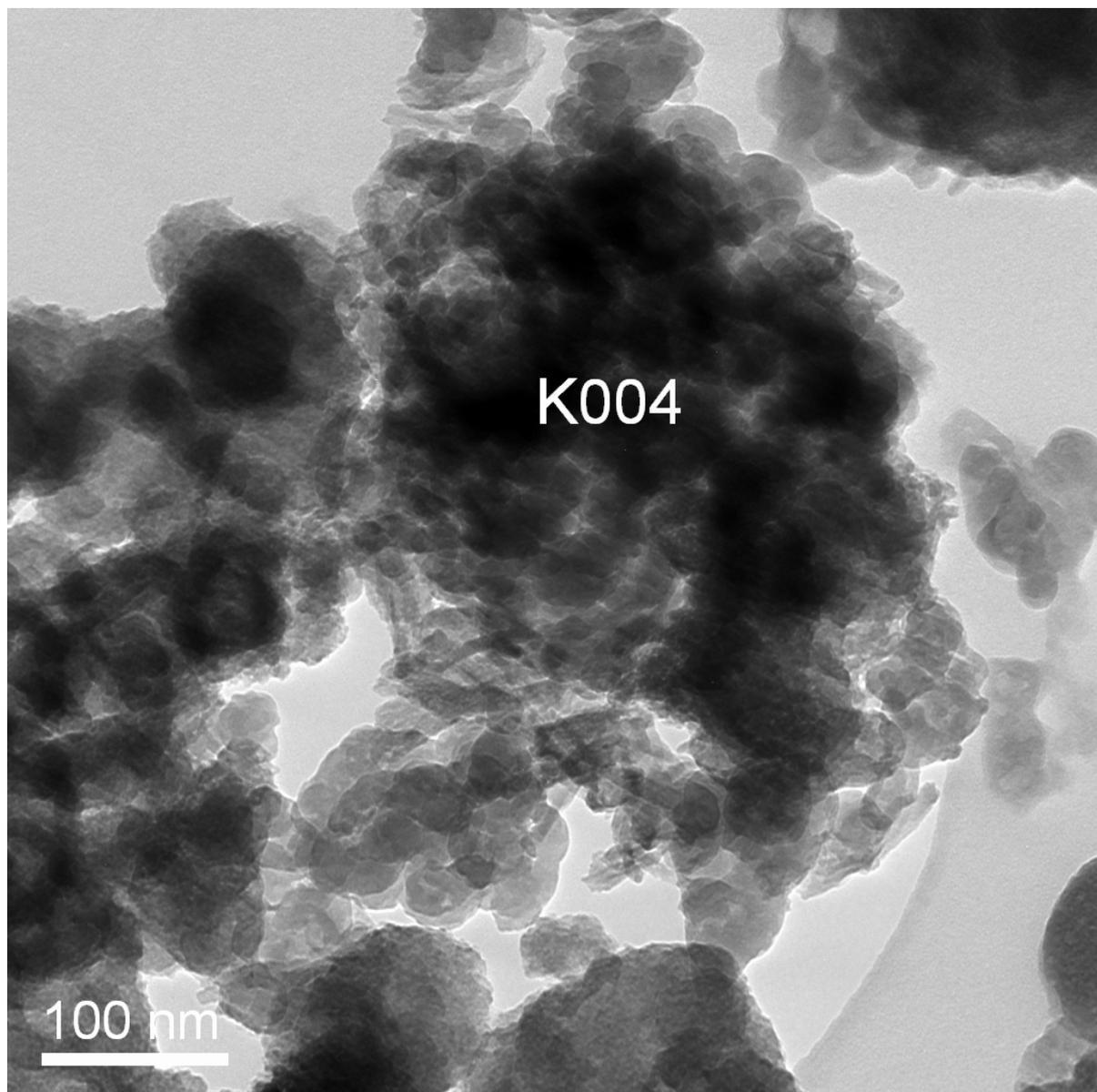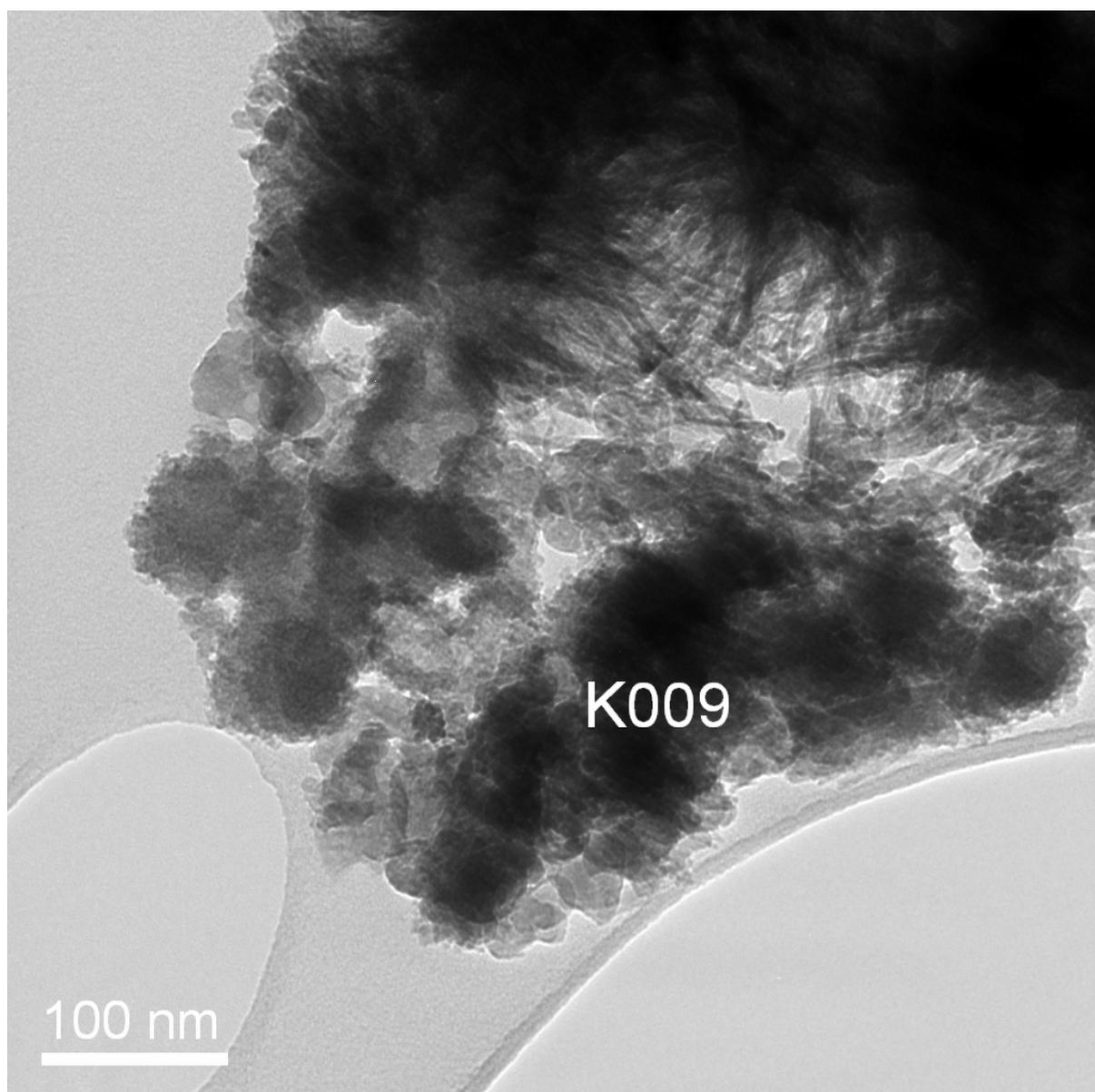
Supplement 7

Scattered electron micrograph from the solid phase of mine waters at Whittle, lagoon 2

Mag = 100.00 K X	200nm	EHT = 3.00 kV	Signal A = InLens	Date :6 Mar 2008
		WD = 3 mm	Photo No. = 29	Time :11:40:11

Supplement 8

High resolution transmitted electron micrographs from the solid phase of influent 2 (Bowden Close, k004: Al-S hydroxide, k009: Fe-Al hydroxide)

Supplement 9

a) AFM plot from solid phases of 0.45 µm filtered mine water sampled at Shilbottle; length of lower frame side = 5 µm; b) FT-IR spectra for selected mine water precipitates from Acomb (AC), Bowden Close (BC), Quaking Houses (QH), Shilbottle (SB) and Whittle (WH);