

## Supporting Information

## 2 Arsenic and phosphorus association with iron nanoparticles between streams 3 and aquifers: implications for arsenic mobility

4 Adam Hartland<sup>a</sup>, Joshua R. Larsen<sup>b</sup>, Martin S. Andersen<sup>c</sup>, Mohammed Baalousha<sup>d</sup>, Denis  
5 O'Carroll<sup>c</sup>

<sup>6</sup> Environmental Research Institute, School of Science, Faculty of Science and Engineering,  
<sup>7</sup> University of Waikato, Hamilton, New Zealand

<sup>b</sup>School of Geography, Planning and Environmental Management, The University of Queensland, Australia

<sup>10</sup> Connected Waters Initiative Research Centre, UNSW Australia, 110 King Street, Manly Vale,  
<sup>11</sup> NSW 2093, Australia

12      <sup>d</sup>Centre for Environmental NanoScience and Risk, Arnold School of Public Health, University of  
13      South Carolina, USA

14 Summary

**16 Pages S1-S13 contain supporting information comprising 6 Figures, 4 Tables and 1 equation.**

**Figure S1.** The location of this study at Elfin Crossing, Maules Creek, a tributary of the Namoi River, located on the western slopes of the Great Dividing Range NSW, Australia.

**Table S1.** Physicochemical data from flow cell monitoring of pumped groundwater.

**Table S2.** Pooled standard deviations for elemental concentrations in operationally defined fractions determined in this study.

22 **Table S3.** Concentrations of iron (Fe), phosphorus (P), arsenic (As) and vanadium (V) in  
23 fractionated water samples from Maules Creek. Concentrations for EC7, EC4, E3 and E4 are the  
24 averages and standard deviations from the analysis of procedural duplicates. Data from the other  
25 piezometers sampled are single analyses. For the estimated pooled error associated with  
26 fractionation and ICPMS analysis see Table 1.

**Figure S2.** Typical AFM images at different scales of 5  $\mu\text{m} \times 5 \mu\text{m}$ , 3  $\mu\text{m} \times 3 \mu\text{m}$ , 2  $\mu\text{m} \times 2 \mu\text{m}$  and 1  $\mu\text{m} \times 1 \mu\text{m}$ .

**Figure S3.** AFM size distribution together with a Log-normal distribution fit of (a) Hyp 1, (b) Hyp 2, (c) Hyp 3, (d) F4, (e) MBH and (f) River.

**Figure S4.** (a) Relationship between the total iron (Fe) concentration and the Fe concentration in fractionated samples (Fe > 1 kDa nominal pore size [○]; Fe removed by ENV+ resin [●]). (b) Relationship between the Fe concentration in the colloidal size range (>1 kDa nominal pore size)

34 in water samples and Fe removed by ENV+ resin. Least squares fits shown by red lines. Error  
35 bars are the cumulative pooled standard deviations determined from four replicated procedural  
36 analyses.

37 **Figure S5.** The relationship between total colloidal ( $> 1$  kDa) oxyanion concentration  
38 [phosphorus (P) + arsenic (As) + vanadium (V)] and the colloidal Fe concentration in water  
39 samples.

40 **Figure S6.** Reanalysis of Bangladeshi groundwater data from Garnier et al. [Ref-22]. (a)  
41 Relationship between Fe concentration in the 100 – 10 kDa fraction and phosphorus (P), and (b)  
42 arsenic (As) in the same fraction. (c) Relationship between colloidal P and nominally dissolved  
43 As, and (d) between colloidal As and nominally dissolved P. These data show similar  
44 relationships exist between colloidal Fe, As and P in Bangladeshi groundwater and imply that  
45 competitive interactions between P and As for colloidal iron carriers in groundwater are a  
46 widespread phenomenon.

47 **Table S4.** Summary of model parameters used for the determination of nanoparticle travel  
48 distance.

49 **Equation S1** The correlation equation of Nelson & Ginn (Ref-39).

50

51

52

53

54

55

56

57

58

59

60

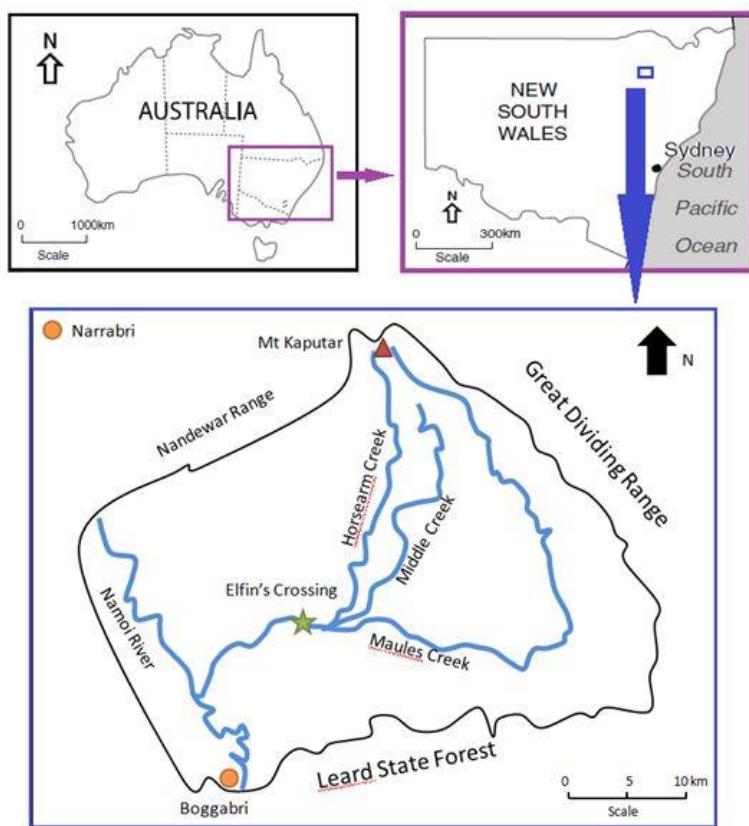
61

62

63

64

65



66

67 **Figure S1.** The location of this study at Elfin Crossing, Maules Creek, a tributary of the Namoi  
68 River, located on the western slopes of the Great Dividing Range NSW, Australia.

69

70

71

72

73

74

75

76

77

78 **Table S1.** Physiochemical data from flow cell monitoring of pumped groundwater.

Bore	date	time	O <sub>2</sub> (mg L <sup>-1</sup> )	EC (µS cm <sup>-2</sup> )	pH	Temp (°C)	Comment
EC7	15/04/2012	8:20	0.68	467	6.49	20	
EC7	15/04/2012	8:20	0.26	454	6.89	19.8	samples taken (majors)
EC7	15/04/2012	8:20	0.21	448	6.69	19.9	samples taken (colloid fractions)
EC4	13/04/2012	11:22	0	440	6.4	22.1	
EC4	13/04/2012	11:28	0	443	6.52	21.8	
EC4	13/04/2012	11:31	0	443	6.58	21.8	samples taken (majors)
EC4	13/04/2012	11:35	0	440	6.66	22.1	samples taken (colloid fractions)
E3	13/04/2012	13:00	0.17	389	6.9	21.48	
E3	13/04/2012	13:10	0.11	398	6.89	21.7	
E4	13/04/2012	14:00	0.08	425	6.93	22.2	
E4	13/04/2012	14:00	0.07	424	6.91	22.1	
E4	13/04/2012	14:00	0.09	423	6.91	22.1	
EC3	14/04/2012	9:40	0.02	415	6.85	21.8	
EC3	14/04/2012	11:00	0	406	6.88	23	
River	14/04/2012	13:10	1.68	447	7.37	20.8	
River	14/04/2012	13:15	1.73	445	7.39	20.8	
River	15/04/2012	8:40	5.95	437	7.14	19.3	
Hyp1 (1.5m)	14/04/2012	12:30	0.1	485	6.91	22	
Hyp1 (1.5m)	14/04/2012	12:40	0.09	484	6.93	21.7	
Hyp2 (0.5m)	14/04/2012	13:30	0.05	458	7.19	21.2	
Hyp2 (0.5m)	14/04/2012	13:35	0.04	458	7.19	21.1	
Hyp3 (1m)	14/04/2012	15:00	0	467	6.96	22.1	
Hyp3 (1m)	14/04/2012	15:15	0	467	6.99	21.8	
MBH13 (6.75m)	14/04/2012	16:56	0.22	343	6.95	21.8	
MBH13 (6.75m)	14/04/2012	17:12	0.15	342	6.95	21.7	SWL = 5.27m
EC8	15/04/2012	9:30	0.22	491	6.74	21.2	
EC8	15/04/2012	9:45	0.19	491	6.77	21.4	
EC8	15/04/2012	9:53	0.3	492	6.78	21.5	SWL = 1.755m

79

80

81

83 **Table S2.** Pooled standard deviations for elemental concentrations in operationally defined  
 84 fractions determined in this study.

Fraction	$\pm$ ( $\mu\text{g L}^{-1}$ )				$\pm$ (RSD%)			
	Fe	P	As	V	Fe	P	As	V
Total	4.94	0.15	0.24	1.79	0.44	0.07	0.01	0.25
< 100 kDa	24.99	0.16	0.07	0.90	2.39	0.07	0.00	0.13
< 10 kDa	15.98	0.56	0.10	0.52	1.98	0.32	0.00	0.08
< 1 kDa (truly dissolved)	50.19	0.27	0.34	1.44	13.96	0.23	0.01	0.22
ENV+	209.22	2.01	0.69	2.02	59.23	1.05	0.02	0.34
Colloidal (total-1 kDa)	50.43	0.31	0.42	2.30	4.52	0.13	0.01	0.32
Coarse colloidal (total - 100 kDa)	25.47	0.22	0.25	2.01	2.28	0.09	0.01	0.28
Nanoparticulate (100 - 1 kDa)	56.06	0.31	0.35	1.70	5.02	0.13	0.01	0.23
Nanoparticulate (100 - 10 kDa)	29.66	0.59	0.12	1.04	2.66	0.25	0.00	0.14
Fine nanoparticulate (10 - 1 kDa)	52.67	0.62	0.36	1.53	4.72	0.27	0.01	0.21
Organic associated (total-ENV+)	209.28	2.02	0.73	2.70	18.75	0.86	0.02	0.37

86 **Table S3.** Concentrations of iron (Fe), phosphorus (P), arsenic (As) and vanadium (V) in fractionated water samples from Maules  
 87 Creek. Concentrations for EC7, EC4, E3 and E4 are the averages and standard deviations from the analysis of procedural duplicates.  
 88 Data from the other piezometers sampled are single analyses. For the estimated pooled error associated with fractionation and ICPMS  
 89 analysis see Table 1.

Piezometer	Depth (m)	Concentration ( $\mu\text{mol L}^{-1}$ )					Concentration ( $\mu\text{mol L}^{-1}$ )				
		Fe (total)	Fe (< 100 kDa)	Fe (< 10 kDa)	Fe (< 1 kDa)	Fe (ENV+)	P (total)	P (< 100 kDa)	P (< 10 kDa)	P (< 1 kDa)	P (ENV+)
EC7		57.6 $\pm$ 0.1	54.9 $\pm$ 0.9	44.1 $\pm$ 0.2	21.9 $\pm$ 1.7	17.5 $\pm$ 7.3	9.4 $\pm$ 0.2	8.6 $\pm$ 0.2	5.0 $\pm$ 0.6	1.0 $\pm$ 0.5	5.0 $\pm$ 0.6
EC4		18.9 $\pm$ 0.2	17.6 $\pm$ 0.2	12.4 $\pm$ 0.5	3.4 $\pm$ 0.5	6.9 $\pm$ 1.5	8.4 $\pm$ 0.2	8.1 $\pm$ 0.0	6.0 $\pm$ 0.1	3.1 $\pm$ 0.2	5.6 $\pm$ 0.7
E3		1.1 $\pm$ 0.0	0.5 $\pm$ 0.0	0.4 $\pm$ 0.2	0.2 $\pm$ 0.1	0.3 $\pm$ 0.0	3.3 $\pm$ 0.0	3.3 $\pm$ 0.1	3.2 $\pm$ 0.3	3.2 $\pm$ 0.2	3.2 $\pm$ 0.1
E4		2.3 $\pm$ 0.0	1.9 $\pm$ 0.1	1.0 $\pm$ 0.0	0.3 $\pm$ 0.2	0.6 $\pm$ 0.2	9.1 $\pm$ 0.0	8.9 $\pm$ 0.2	8.4 $\pm$ 0.9	7.9 $\pm$ 0.1	11.0 $\pm$ 3.9
EC3		4.8	2.2	1.3	0.1	1.5	8.7	7.6	6.9	4.5	8.2
River		3.2	0.2	0.1	0.0	1.6	3.7	3.6	3.5	0.0	4.0
HYP1	0.5	3.4	0.2	0.2	0.1	1.9	4.5	3.8	3.7	2.7	3.7
HYP2	1	83.0	78.0	51.8	18.9	33.4	11.8	9.7	3.3	0.9	7.4
HYP3	1.5	88.6	0.1	0.4	0.0	1.8	4.8	3.8	3.3	0.0	4.1
MCBH		1.8	1.8	0.2	0.1	1.5	6.1	5.3	4.1	4.4	4.8
EC8		2.4	72.4	35.0	4.1	29.1	10.6	8.8	2.9	1.5	4.5
Concentration (nmol L $^{-1}$ )											
Piezometer	Depth (m)	As (total)	As (< 100 kDa)	As (< 10 kDa)	As (< 1 kDa)	As (ENV+)	V (total)	V (< 100 kDa)	V (< 10 kDa)	V (< 1 kDa)	V (org)
EC7		65.8 $\pm$ 3.0	69.9 $\pm$ 0.1	65.5 $\pm$ 0.6	61.9 $\pm$ 4.1	64.4 $\pm$ 2.6	7.7 $\pm$ 0.5	6.1 $\pm$ 0.5	5.7 $\pm$ 0.8	4.4 $\pm$ 0.4	4.6 $\pm$ 0.1
EC4		56.2 $\pm$ 4.3	57.8 $\pm$ 1.3	55.6 $\pm$ 1.6	63.0 $\pm$ 3.0	59.5 $\pm$ 9.8	7.1 $\pm$ 1.7	6.6 $\pm$ 0.2	6.1 $\pm$ 0.3	6.1 $\pm$ 0.7	5.1 $\pm$ 1.3
E3		15.9 $\pm$ 0.3	14.3 $\pm$ 0.9	14.9 $\pm$ 1.6	14.7 $\pm$ 2.3	13.2 $\pm$ 1.7	34.9 $\pm$ 3.1	33.8 $\pm$ 1.7	30.6 $\pm$ 0.5	33.0 $\pm$ 2.7	29.3 $\pm$ 3.8
E4		54.1 $\pm$ 3.5	49.4 $\pm$ 0.9	49.1 $\pm$ 1.2	46.0 $\pm$ 7.3	60.3 $\pm$ 15.3	7.2 $\pm$ 0.1	9.1 $\pm$ 0.5	7.3 $\pm$ 0.2	8.3 $\pm$ 0.4	8.0 $\pm$ 0.6
EC3		43.9	46.0	40.9	34.9	44.8	11.7	8.4	5.4	6.0	6.5
River		13.6	20.3	19.3	0.0	19.0	44.6	58.7	59.1	0.0	57.5
HYP1	0.5	19.5	20.7	16.1	11.7	19.1	60.8	62.5	54.8	41.0	49.2
HYP2	1	100.9	102.8	92.3	81.2	99.7	11.2	9.0	7.2	3.7	8.3
HYP3	1.5	18.1	19.9	15.8	0.0	19.6	65.4	56.9	47.4	0.0	64.2
MCBH		52.4	49.8	40.9	49.0	44.0	23.9	19.0	15.3	21.9	15.7
EC8		86.0	87.2	62.9	44.5	72.6	13.0	10.4	6.8	2.2	11.2

91 **Table S5.** Dissolved organic carbon (DOC) d<sup>13</sup>C data from pumped groundwater samples.  
 92 For piezometer locations see Figure 2 in main text.

93

Piezometer	Date	DOC (mg L <sup>-1</sup> )	$\delta^{13}\text{C}$
E3	13/04/201 2	0.54	-11.2
E3	13/04/201 2	0.53	-11.6
E4	13/04/201 2	2.14	-22.0
EC3	14/04/201 2	2.29	-20.5
EC4d	13/04/201 2	1.91	-20.0
EC7	13/04/201 2	1.88	-20.0
EC8	15/04/201 2	1.82	-19.4
HYP3 1.5	14/04/201 2	2.27	-20.9
HYP1 0.5	14/04/201 2	2.36	-22.3
HYP2 1.0	14/04/201 2	2.28	-21.4
MBH	14/04/201 2	1.97	-19.7
MBH	14/04/201 2	1.93	-23.0
River	14/04/201 2	1.72	-20.5
River	15/04/201 2	1.70	-20.7

94

95

96

97

98

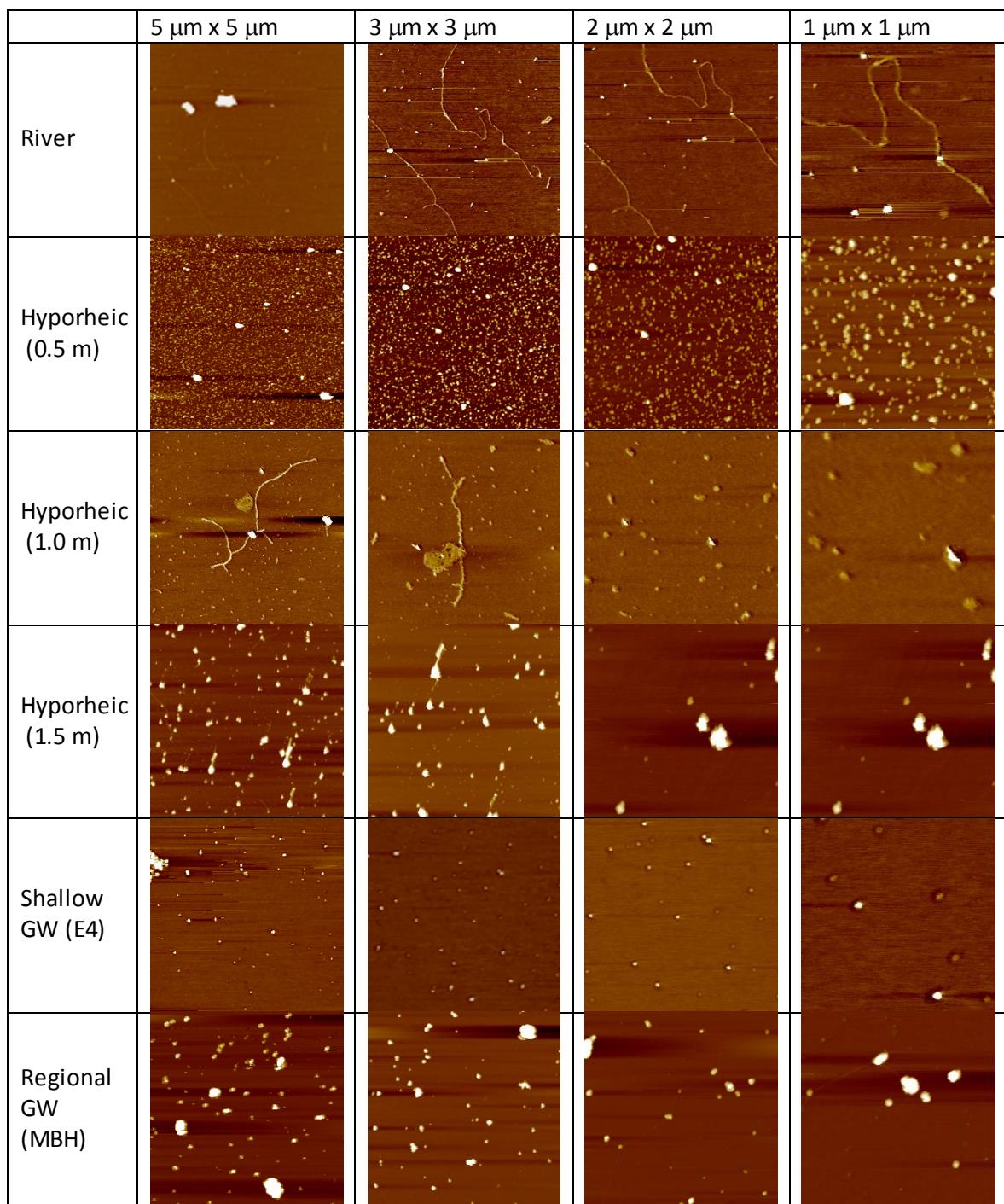
99

100

101

102

103



104

105 **Figure S2.** Typical AFM images at different scales of 5  $\mu\text{m} \times 5 \mu\text{m}$ , 3  $\mu\text{m} \times 3 \mu\text{m}$ , 2  $\mu\text{m} \times 2 \mu\text{m}$  and 1  $\mu\text{m} \times 1 \mu\text{m}$ .

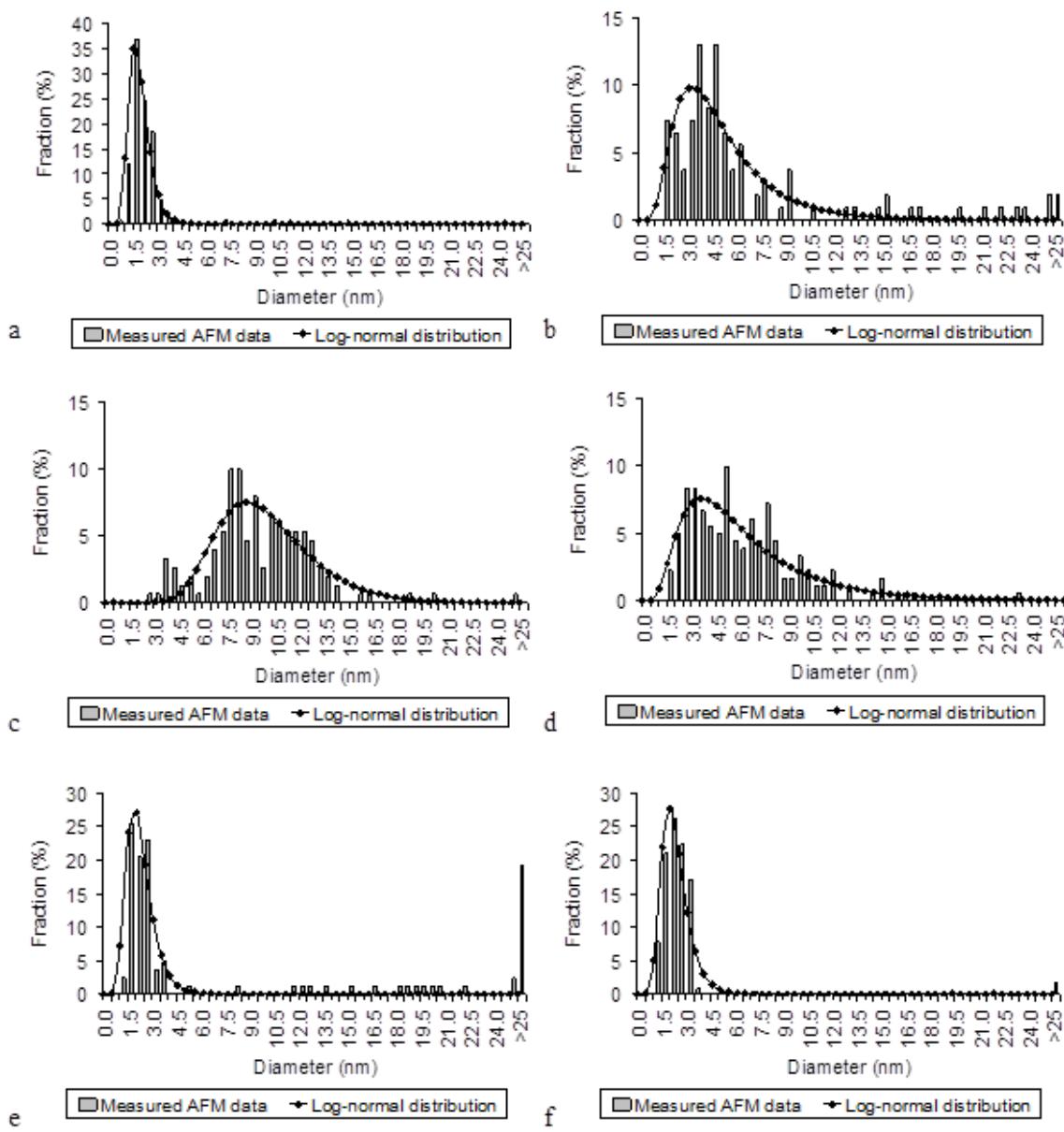
107

108

109

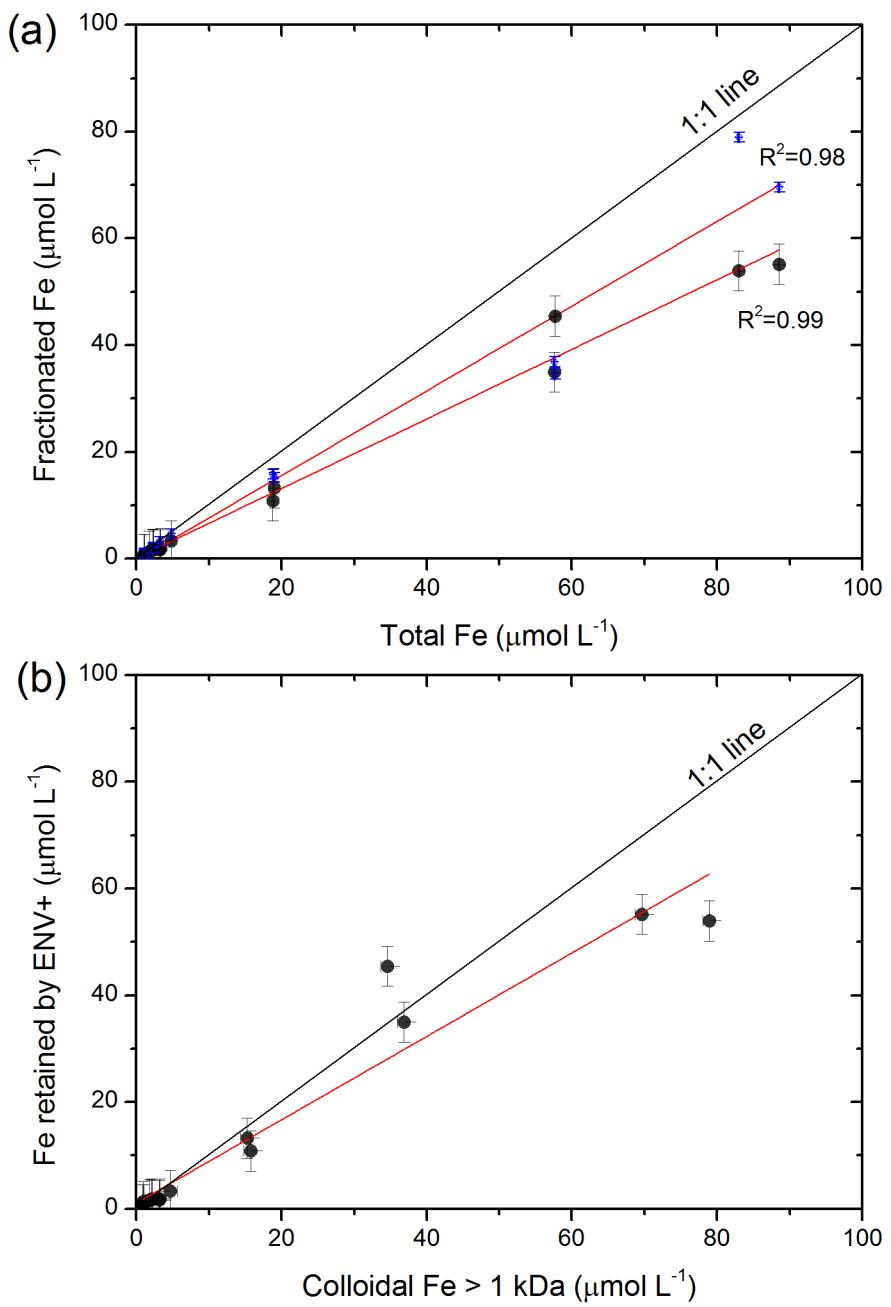
110

111



112

113 **Figure S3.** AFM size distribution together with a Log-normal distribution fit of (a) Hyp 1, (b) Hyp 2,  
114 (c) Hyp 3, (d) E4, (e) MBH and (f) River.

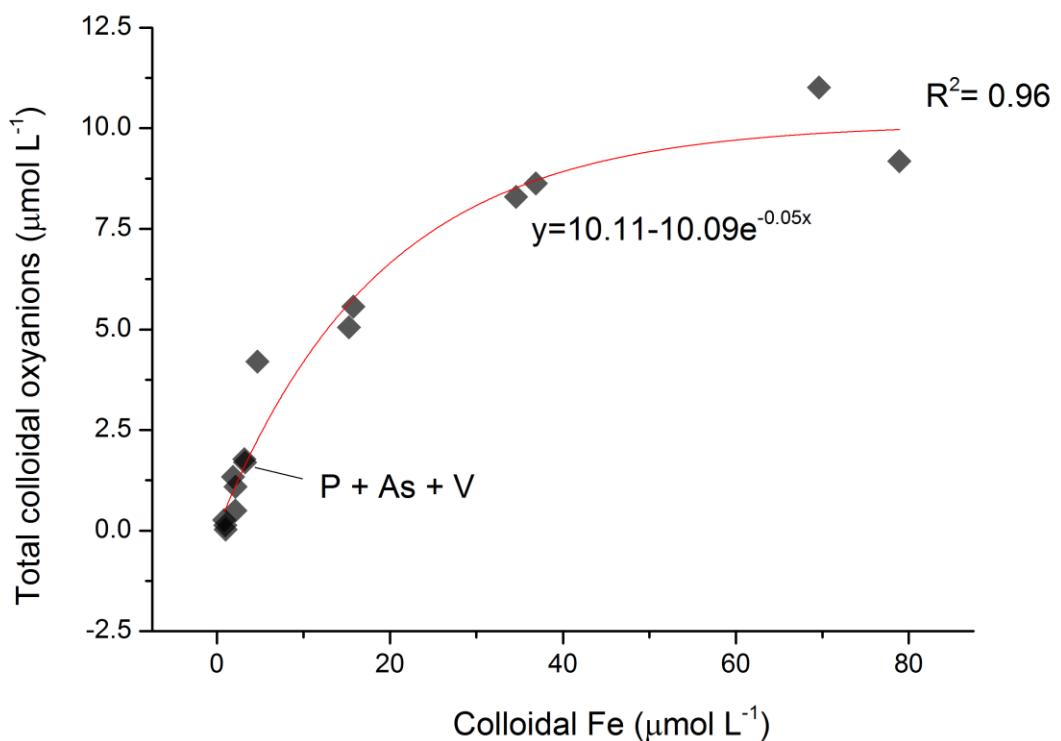


115

116 **Figure S4.** (a) Relationship between the total iron (Fe) concentration and the Fe  
 117 concentration in fractionated samples (Fe  $> 1 \text{ kDa}$  nominal pore size [●]; Fe removed by  
 118 ENV+ resin [○]). (b) Relationship between the Fe concentration in the colloidal size range  
 119 ( $> 1 \text{ kDa}$  nominal pore size) in water samples and Fe removed by ENV+ resin. Least squares  
 120 fits shown by red lines. Error bars are the cumulative pooled standard deviations determined  
 121 from four replicated procedural analyses.

122

123

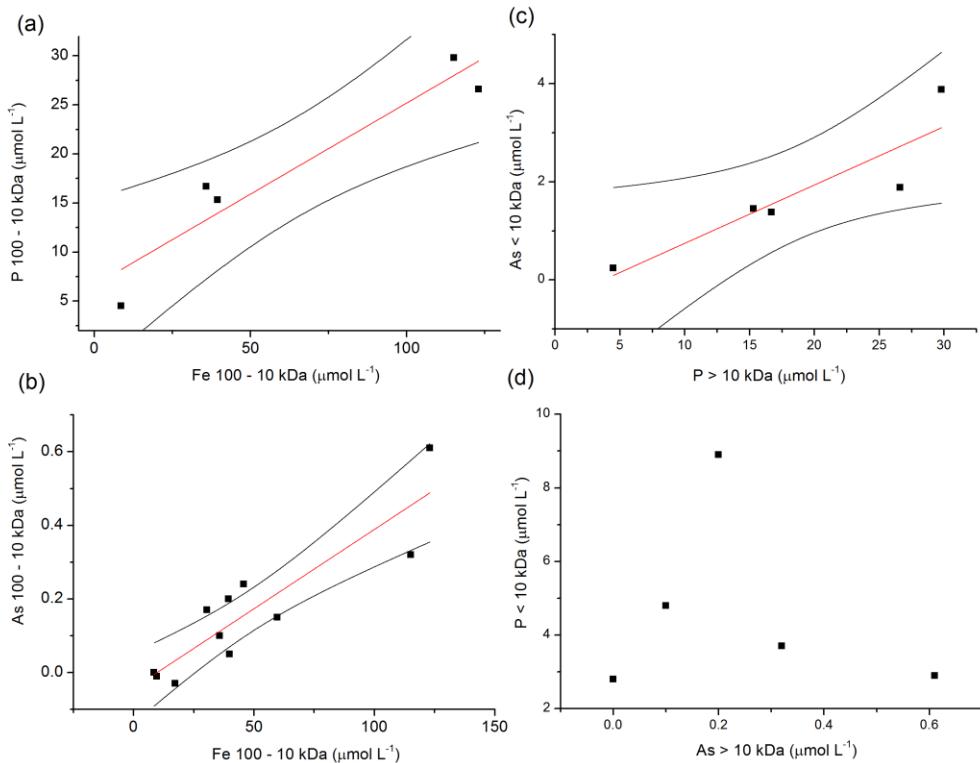


124

125 **Figure S5.** The relationship between total colloidal ( $> 1 \text{ kDa}$ ) oxyanion concentration  
 126 [phosphorus (P) + arsenic (As) + vanadium (V)] and the colloidal Fe concentration in water  
 127 samples.

128

129



130

131

132 **Figure S6.** Reanalysis of Bangladeshi groundwater data from Garnier et al. [Ref-22]. (a)  
 133 Relationship between Fe concentration in the 100 – 10 kDa fraction and phosphorus (P), and  
 134 (b) arsenic (As) in the same fraction. (c) Relationship between colloidal P and nominally  
 135 dissolved As, and (d) between colloidal As and nominally dissolved P. These data show  
 136 similar relationships exist between colloidal Fe, As and P in Bangladeshi groundwater and  
 137 imply that competitive interactions between P and As for colloidal iron carriers in  
 138 groundwater are a widespread phenomenon.

139

140 **Table S5.** Summary of model parameters used for the determination of nanoparticle travel  
 141 distance

Nanoparticle particle radius (m)	$50 \times 10^{-9}$
Collector (sand grain) radius (m)	$1 \times 10^{-3}$
Water Velocity (m/s)	$1.4 \times 10^{-6}$
Fluid Viscosity (Pa s)	$1.03 \times 10^{-3}$
Fluid Density ( $\text{kg/m}^3$ )	$1 \times 10^3$
Particle Density ( $\text{kg/m}^3$ )	$3 \times 10^3$
Hamaker Constant (J)	$2.1 \times 10^{-20}$
Temperature ( $^\circ\text{C}$ )	20
Porosity (e)	0.36
Attachment efficiency ( $\alpha$ )	0.01

142

143

144    **Equation S1** The correlation equation of Nelson & Ginn (Ref-39).

$$145 \quad \eta \approx \gamma^2 \left[ 2.4 A_s^{\frac{1}{3}} \left( \frac{N_{Pe}}{N_{Pe} + 16} \right)^{0.75} N_{Pe}^{-0.68} N_{LO}^{0.015} N_{Gi}^{0.8} + A_s N_{LO}^{1/8} N_R^{15/8} + 0.7 \left( \frac{N_{Gi}}{N_{Gi} + 0.9} \right) N_G N_R^{-0.05} \right]$$

$A_s$                  = porosity dependent parameter  $= 2(1 - \gamma^5)/(2 - 3\gamma + 3\gamma^5 - 2\gamma^6)$   
 $\gamma$                   $= (1 - n)^{1/3}$   
 $N_{Pe}$                  = Peclet number  $= U d_c / D_{BM}$   
 $D_{BM}$                  = Brownian diffusion coefficient for a sphere in an infinite fluid (from Stokes-Einstein equation:  $D_{BM} = \frac{k_B T}{3\pi\mu d_p}$ )  
 $k_B$                  = Boltzmann constant ( $\sim 1.38 \times 10^{-23} \text{ m}^2 \cdot \text{kg} \cdot \text{s}^2 \cdot \text{K}^{-1}$ )  
 $\mu$                  = dynamic (absolute) viscosity of fluid  
 $d_p$                  = diameter of colloid  
 $T$                  = temperature  
 $U$                  = approach (or darcy) velocity  $= v \times n$   
 $d_c$                  = diameter of collector  
 $N_{LO}$                  = London number  $= H / (9\pi\mu a_p^2 U)$   
 $H$                  = Hamaker coefficient  
 $a_p$                  = radius of colloid  
 $N_G$                  = gravity number  $= 2a_p^2 (\rho_p - \rho_f) g / (9\mu U)$   
 $N_{Gi}$                   $= 1 / (N_G + 1)$   
 $\rho_f, \rho_p$                  = density of fluid and particle  
 $g$                  = gravitational acceleration, 9.81 m/s  
 $N_R$                  = aspect ratio  $= a_p / a_s$   
 $a_s$                  = radius of collector

146

147