# Targeted Delivery of Nanoparticles to a Heterogeneous Crude Oil Zone in an Unsaturated Porous Medium

## Supplementary Information

Najmeh Jaberi[a,*], Stuart Linley[b], Neil R. Thomson[a]

[a]Department of Civil & Environmental Engineering, University of Waterloo, Waterloo, Ontario, Canada
[b]Now at Yusuf Hamied Department of Chemistry, University of Cambridge, Cambridge, England.

### SI.1. Batch Binding Tests

Batch binding tests were conducted by adding ~15 g of sediment (clean or crude oil-impacted BS) to 20 mL scintillation vials, followed by 10 mL of aqueous nanoparticle suspension (diluted by a factor of 100 with Millipore DI water). The vials were allowed to sit at room temperature for 48 h. The nanoparticle suspension was then collected by filtration (Whatman glass microfiber filter, Grade 934-AH) and analyzed by ICP-OES. All batch tests were performed in triplicate.

Table SI-1. Estimated concentration of CoFe-NP attached to clean and crude-oil impacted Borden sand (BS).

| Material | $S_{max}$ | ±95% CI | |
|---|---|---|---|
| | [mg/kg] | lower limit [mg/kg] | upper limit [mg/kg] |
| BS | 8.2 ± 0.6 | 7.37 | 8.91 |
| 2% wt oil-impacted BS | 25.9 ± 2.1 | 23.57 | 28.32 |
| 4% wt oil-impacted BS | 29.5 ± 2.4 | 26.74 | 32.21 |

Table SI-2(a). Estimated hydraulic parameters (used flow data from the tracer experiment).

| Zone | Material | $\theta_r$ [-] | $\phi_r$ [-] | α [1/m] | $n$ [-] | $K_s$ [m/s]×$10^{-5}$ |
|---|---|---|---|---|---|---|
| 2 | Wet packed BS | 0.06 | 0.3 | 14.0 | 1.30 | 7.2 |
| 3 | Moist BS | 0.06 | 0.32 | 14.0 | 1.30 | 7.2 |
| 4 | 2% wt oil-impacted BS | 0.06 | 0.28 | 15.0 | 1.32 | 1.7 |
| 5 | 4% wt oil-impacted BS | 0.06 | 0.34 | 15.0 | 1.30 | 1.0 |

Table SI-2(b). Estimated hydraulic parameters (used flow data from the CoFe-NP experiment).

| Zone | Material | $\theta_r$ | $\phi_r$ | α | $n$ | $K_s$ |
|---|---|---|---|---|---|---|
| | | [-] | [-] | [1/m] | [-] | [m/s]×$10^{-5}$ |
| 2 | Wet packed BS | 0.06 | 0.31 | 14.0 | 1.30 | 7.2 |
| 3 | Moist BS | 0.06 | 0.32 | 14.0 | 1.30 | 7.2 |
| 4 | 2% wt oil-impacted BS | 0.06 | 0.28 | 15.0 | 1.32 | 1.5 |
| 5 | 4% wt oil-impacted BS | 0.06 | 0.35 | 15.0 | 1.30 | 0.9 |

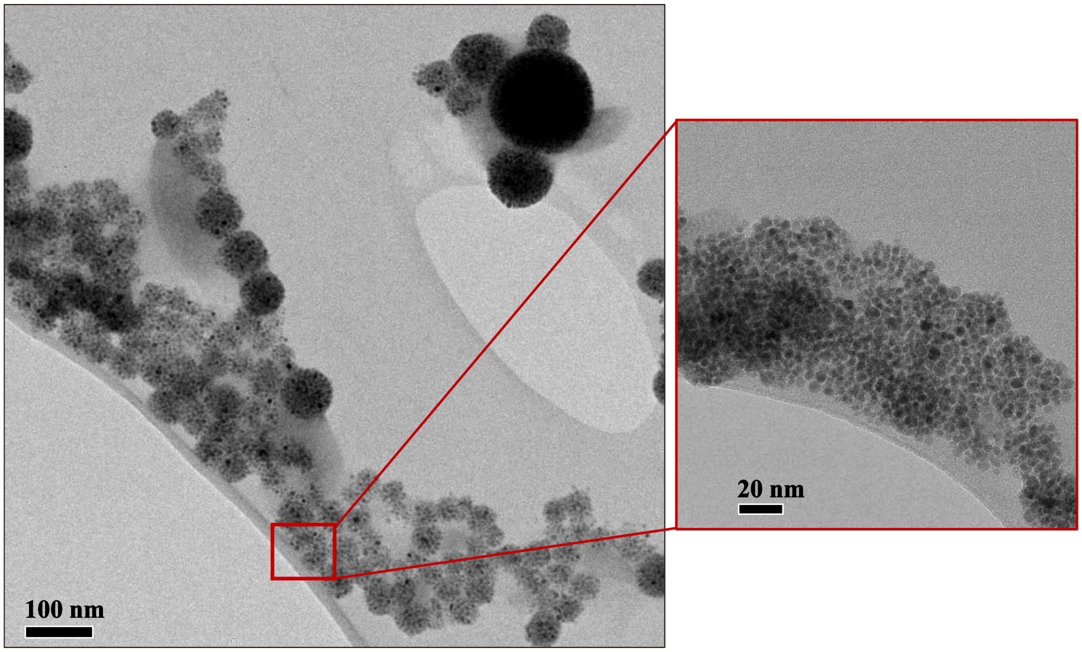


Figure SI-1. TEM images of cobalt iron nanoparticles (CoFe-NPs; 2.5 g/L Pluronic coating concentration) at two magnifications.

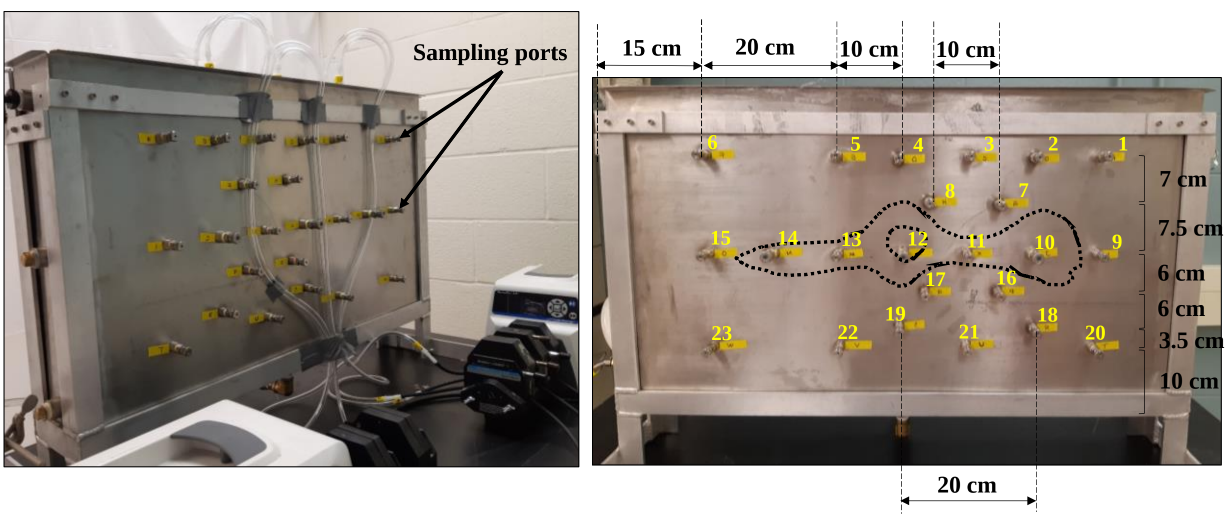


Figure SI-2. Spatial distribution of the sampling ports at the back of the sand tank. Aqueous samples were manually collected during the experiments from each sampling port (every 15 minutes) using a 3-mL syringe with hypodermic needle and then transferred into 5-mL polypropylene cryogenic vials. The dotted line on the right-hand panel indicates approximately where the crude oil impacted BS was emplaced during packing.

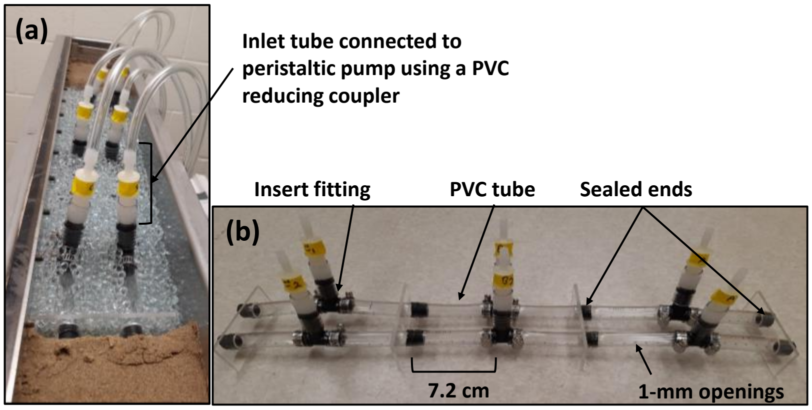


Figure SI-3. (a) An infiltration gallery (46.8 cm long, and ~6-cm thick) constructed at the top of the sand tank comprised of 4 mm glass beads (Fisher Scientific) and (b) a solution release system built from twelve pieces of flexible PVC tubing (1.27 cm ID, 7.2 cm length) with ~1-mm openings drilled at 1-cm increments along the tube length. One end of each tube was sealed using rubber stopers, and the other end attached to a 3.2-mm diameter tubing (inlet) using a tee PVC insert fitting (1 cm ID). All six inlet tubes were connected to two peristaltic pumps (three heads each) to feed the tracer or CoFe-NP aqueous suspension, and water into the system during the experiments.

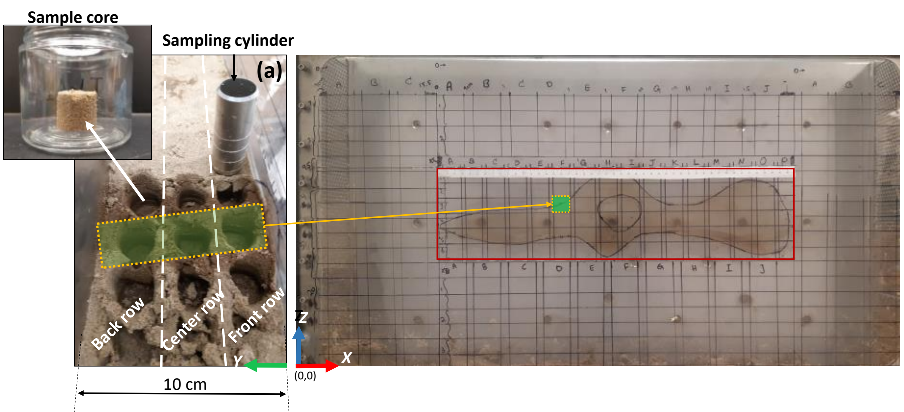


Figure SI-4. (a) Sediment sampling across the 10-cm width of the sand tank from the back row (7.9 cm from the front Plexiglas wall), center row (5.0 cm), and front row (2.1 cm) for a layer at a height of 28 cm from the base of the sand tank. (b) Sampling scheme in the *X*-*Z* plane; 1-cm deep subsamples were collected from the red rectangular box surrounding the crude oil source zone, and 2-cm deep subsamples were collected elsewhere. As an example, subsamples in the green box shown on (a) are related to the location F3 ($X$ = 30 cm, $Z$ = 28 cm) on the sampling grid shown on (b).

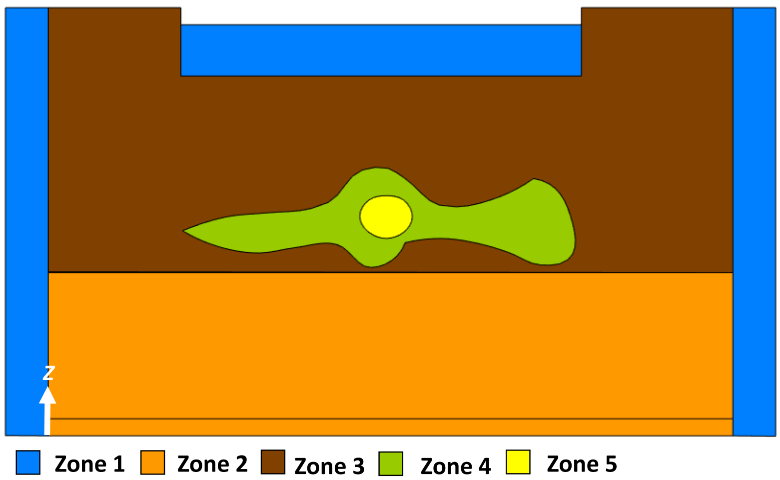


Figure SI-5. The model spatial domain (80 cm long by 50 cm high) was divided into the following five distinct zones: Zone 1, infiltration gallery and the two side chambers filled with glass beads; Zone 2, wet packed BS from *Z* = 0 to 20 cm (denoted as the lower BS zone); Zone 3, moist BS packed from Z =20 to 50 cm (denoted as the upper BS zone); Zone 4, the 2% wt crude oil zone; and Zone 5, the 4% wt crude oil zone.

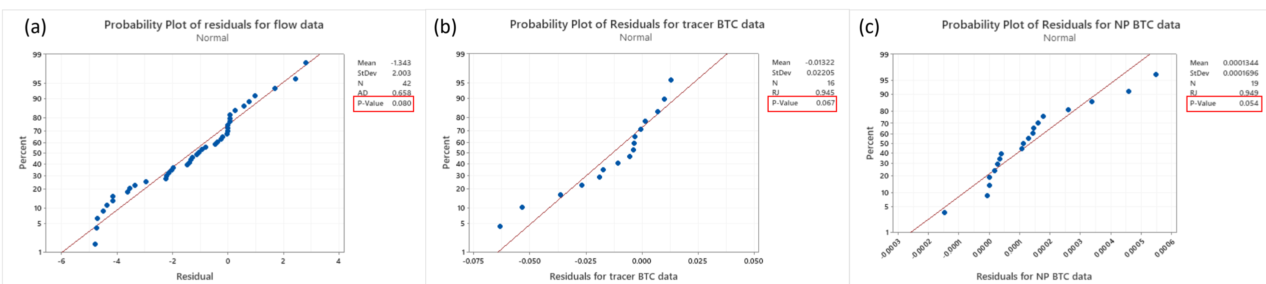


Figure SI-6. Normality test for residuals from (a) outflow data, (b) effluent $Br^-$ data and (c) effluent CoFe-NP data for the tracer and CoFe-NP experiments. Normality was deemed acceptable for a *p*-value > 0.05.

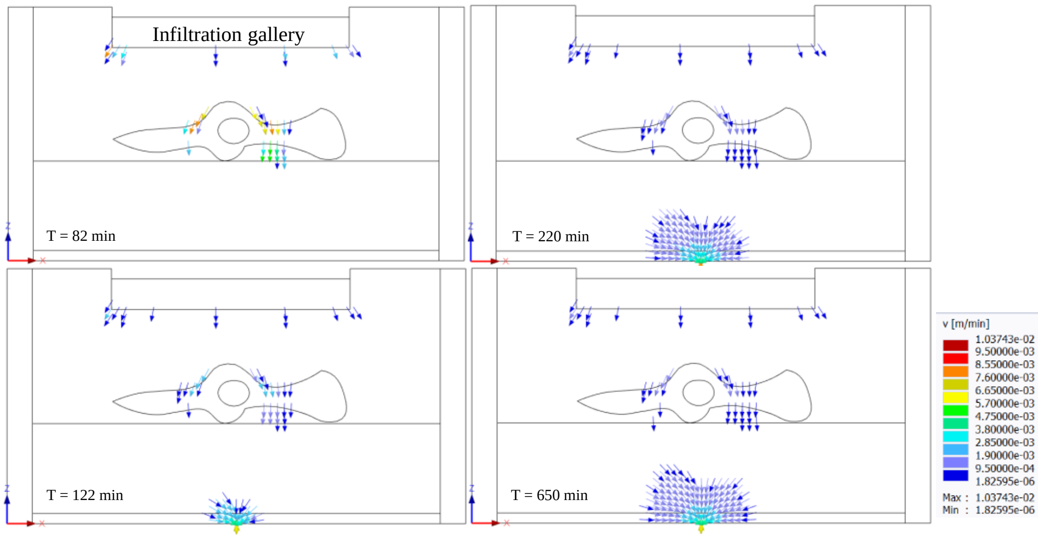


Figure SI-7. Spatial distribution of the simulated Darcy flux at different times during the tracer transport experiment. A similar velocity vector pattern was simulated for the CoFe-NP transport experiment.

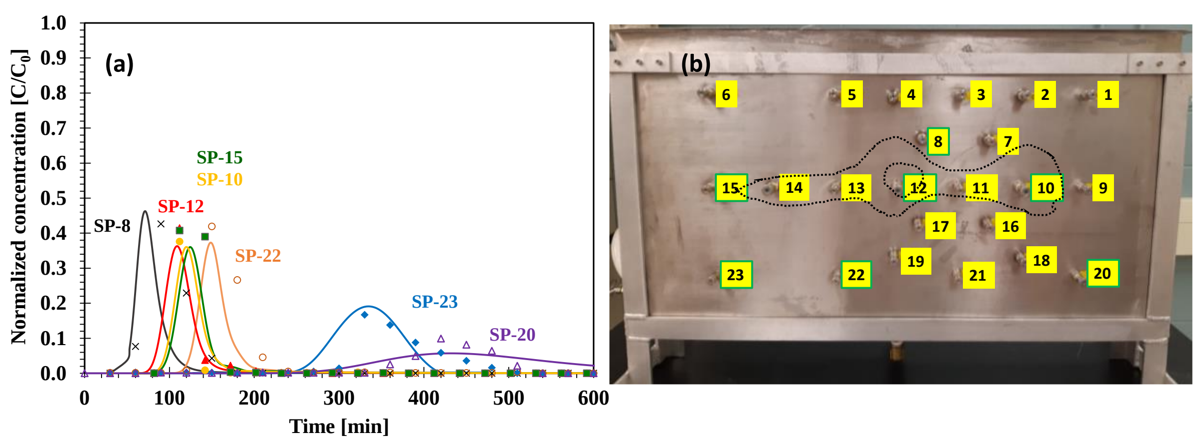


Figure SI-8. (a) Observed (symbols) and simulated (lines) $Br^-$ BTCs at different sampling ports and (b) location of the sampling ports on the back of the sand tank. Data for the other ports are not available due to the clogging of the syringe needles by sand grains.

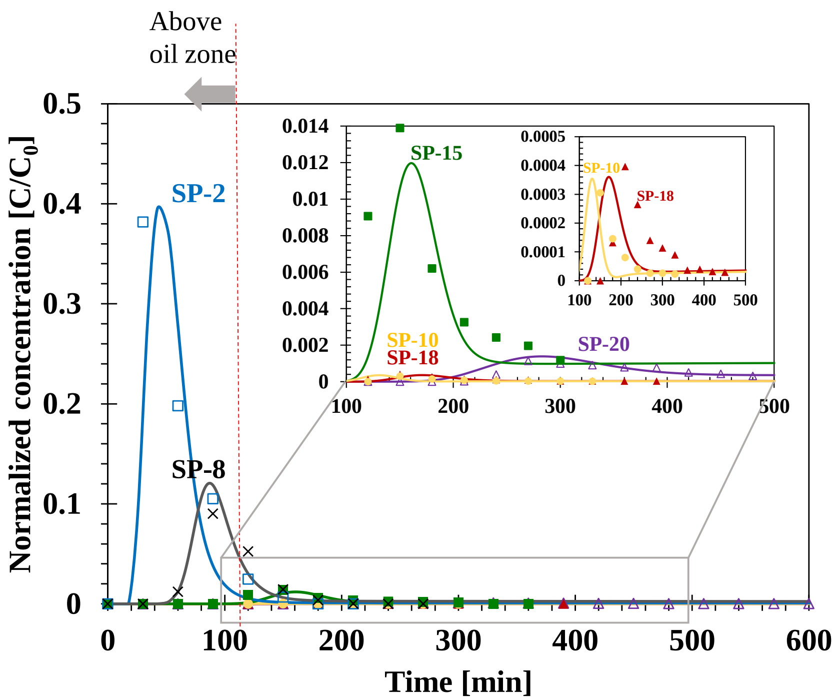


Figure SI-9. Observed (symbols) and simulated (lines) CoFe-NP BTCs at different sampling ports. Data for the other sampling ports is not available due to the clogging of the samplers. SP-2 and SP-8 are located above the crude oil zone, while the remainder are within or below the crude oil zone. See Figure SI-10 for the location of the samplers on the back of the sand tank. Note that inset figures were used to capture the range of normalization concentration observed and simulated.

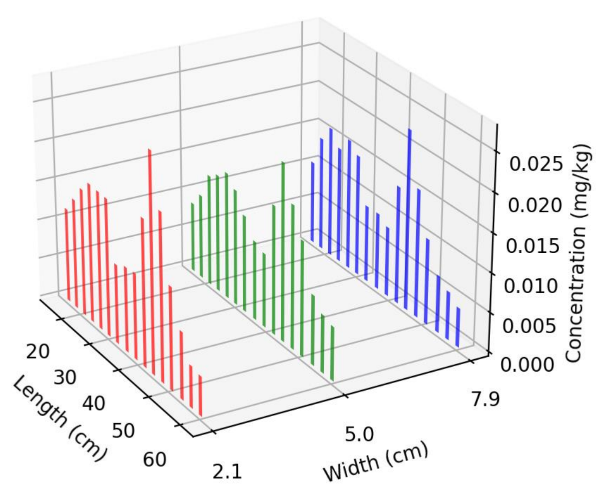


Figure SI-10. An example of the observed concentration of CoFe-NPs retained in subsamples collected across the width of the sand tank (front (2.1 cm), center (5.0 cm) and back (7.9 cm) rows) for a layer at 25.6 cm from the bottom of the tank (i.e, *X* (Length)=16 to 62.4 cm, *Z*=24.6 to 26.6). Width is from the center of the sub-sampling core to the front Plexiglas wall. The concentration of NPs retained is consistent across all rows indicating that preferential transport across the width of the sand tank was insignificant.