In situ remediation of As, Cd, PFOA and PFOS from soil using graphene-based materials

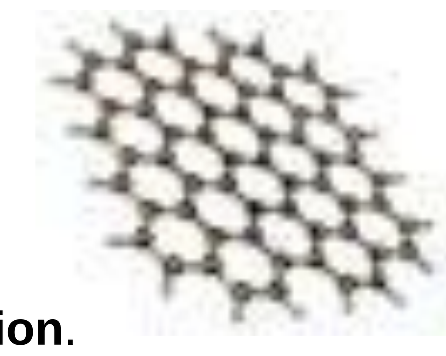
Supriya Lath [1,*], Divina Navarro [1, 2], Dusan Losic [1], Anu Kumar [2], Michael J. McLaughlin [1, 2]

[1] School of Agriculture, Food and Wine, University of Adelaide, Australia. [2] CSIRO, Australia.

Background

Adsorption – common strategy to manage contamination by reducing contaminant mobility and bioavailability, hence alleviating toxicity and risk.

Graphene – novel carbon material; excellent candidate for development as adsorbents due to high surface area and versatile surface chemistry. Demonstrated widely in water/wastewater treatment.



Virtually no studies have investigated the potential of graphene-based materials (GBMs) for ***in situ soil* remediation**.

Aim

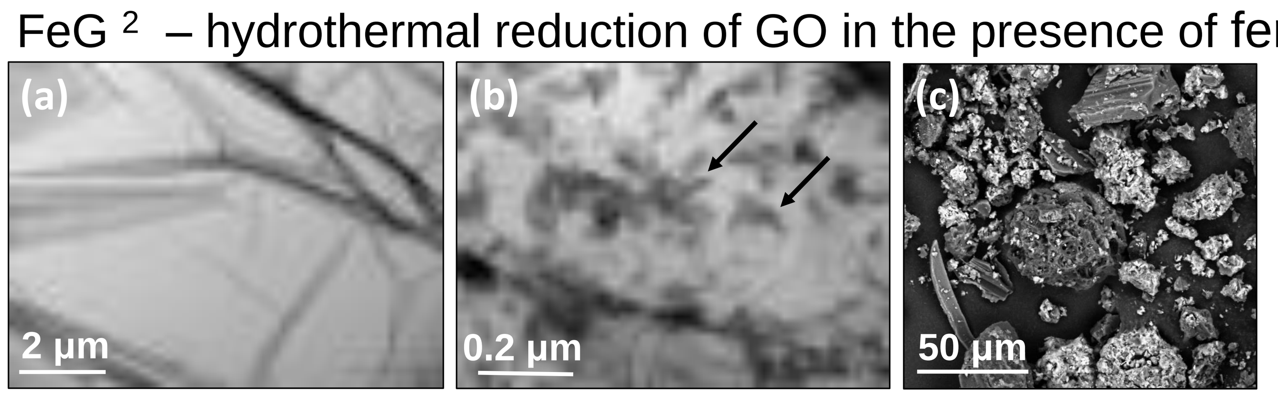
Evaluate the application of GBMs for *in situ* adsorption of soil contaminants.

- Arsenate (**As**), cadmium (**Cd**), perfluorooctanoic acid (**PFOA**) and perfluorooctane sulfonate (**PFOS**)
  → multiple contaminant types (i.e., organic, inorganic, cationic, anionic)
  → singly-contaminated *vs* co-contaminated 'cocktail' soils tested.
- Two GBMs – graphene oxide (**GO**), and an iron-oxide-modified reduced-GO composite (**FeG**) – were chosen; performance was compared with a commercial adsorbent, RemBind™ (**RemB**).
- Chemical and biological assessment of 'remediation':
  → Effect on bioavailability (extractability) of As, Cd, PFOA and PFOS
  → Effect on microbial-mediated soil nitrification function

Experimental Methods

Synthesis of GBMs:

- GO [1] – strong oxidative exfoliation of graphite
- FeG [2] – hydrothermal reduction of GO in the presence of ferrous sulphate



Electron microscopy images of adsorbents:

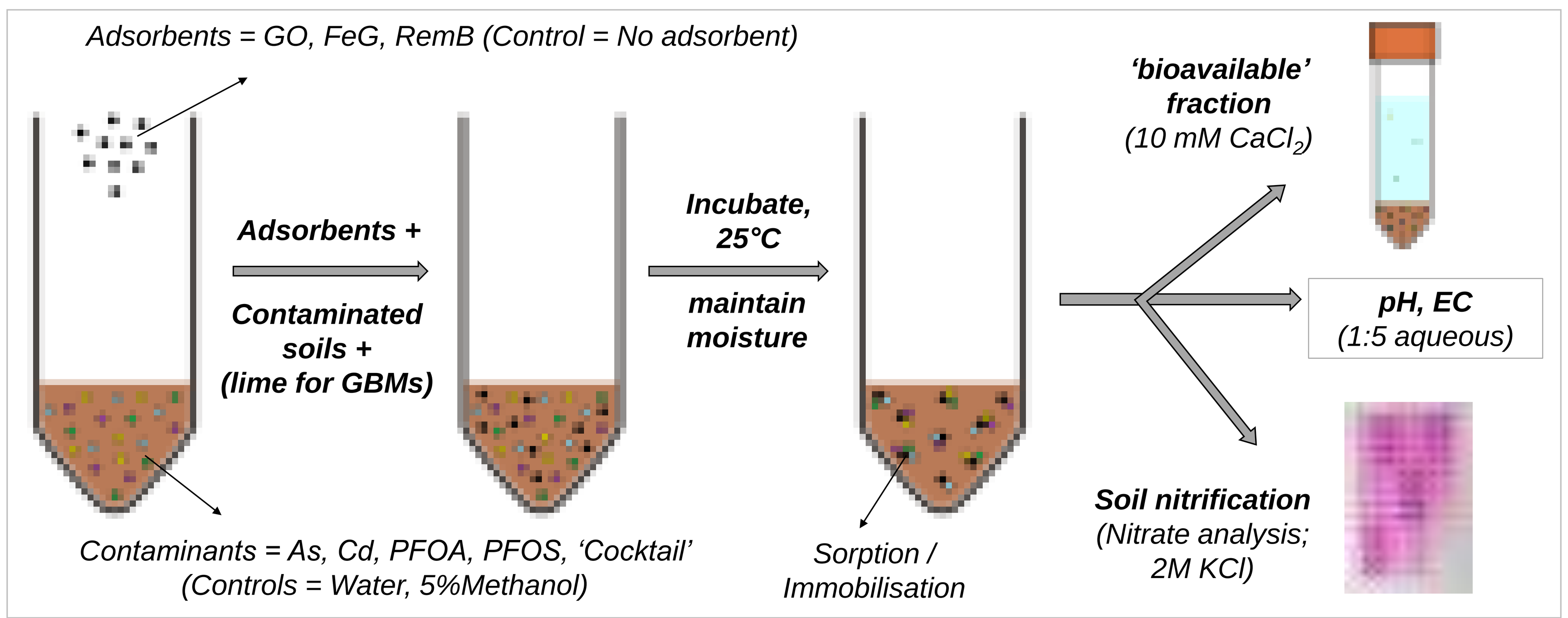
(a) GO
(b) FeG
(c) RemB

Determination of EC50 values for soil nitrification:

- Soil spiking range: As (0.1 – 2500 mg/kg); Cd (0.1 – 1000 mg/kg); PFOA (0.1 – 40 mg/kg); PFOS (0.08 – 225 mg/kg)
- 28 day nitrification incubation test (OECD Test 216)
- Dose-response curves; 50% effect concentrations (EC_{50})

In situ soil remediation trial:

- Contaminant dose based on EC_{50} concentrations for Ad, Cd, PFOA, PFOS
- Singly-contaminated and co-contaminated soils
- Adsorbent dose = 5% w/w
- 'Bioavailable' fractions = 10 mM $CaCl_2$ extracts
- Soil nitrification response = 2 M KCl extracts (nitrate analysis)

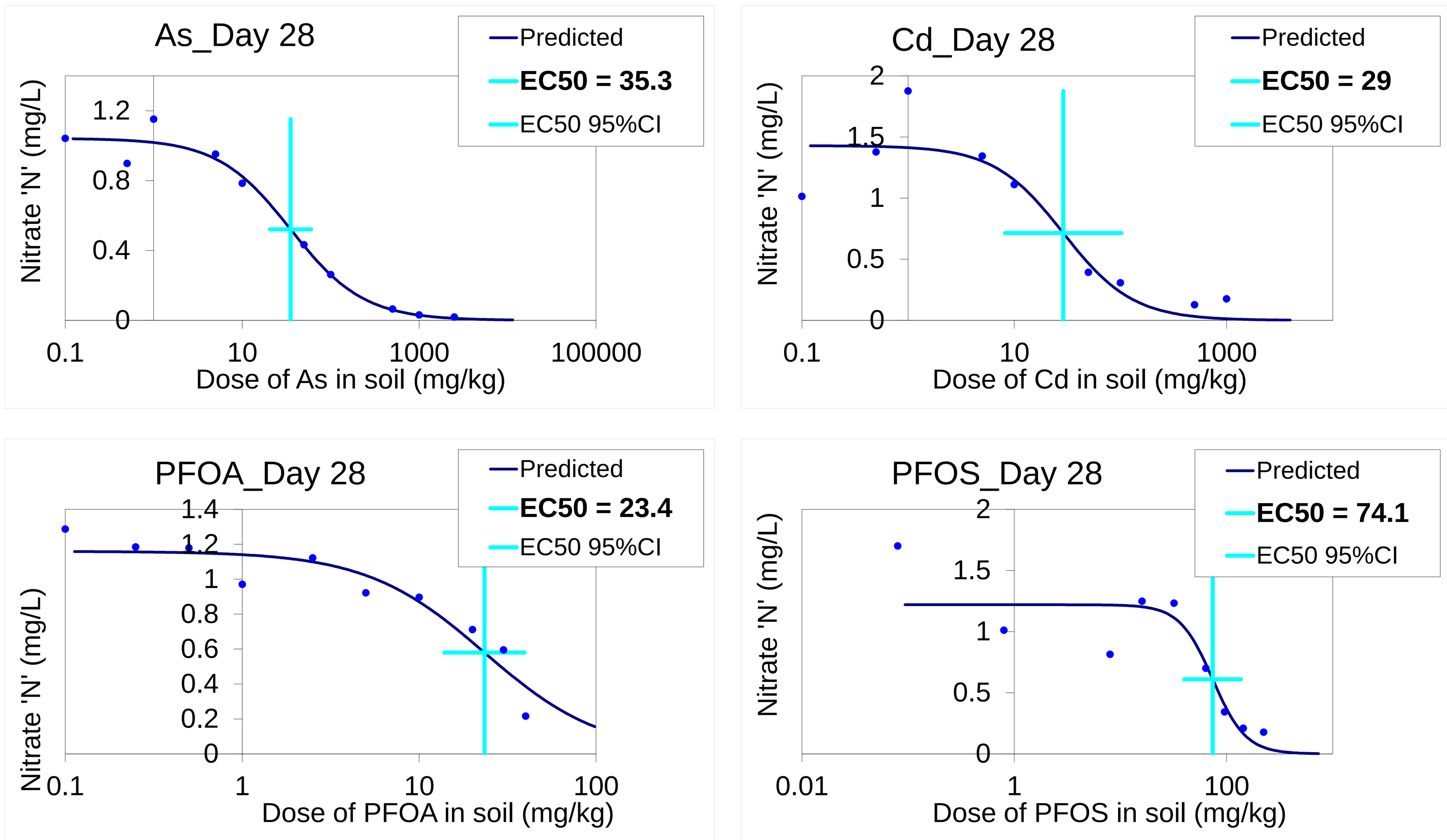


Analysis:

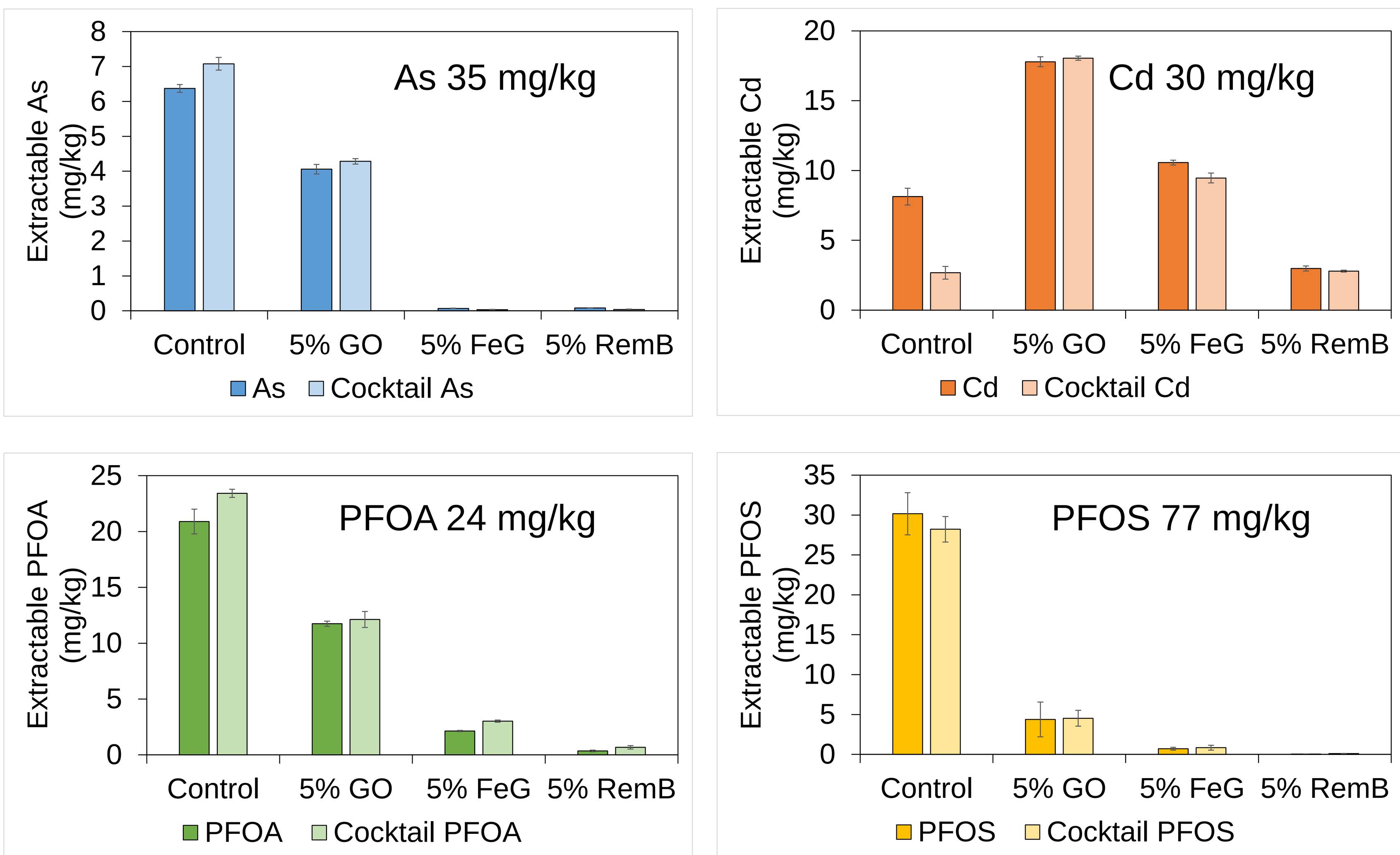
- ICP-OES (Cd, As); LC-MS/MS (PFOA, PFOS); UV-visible spectrophotometry

Results

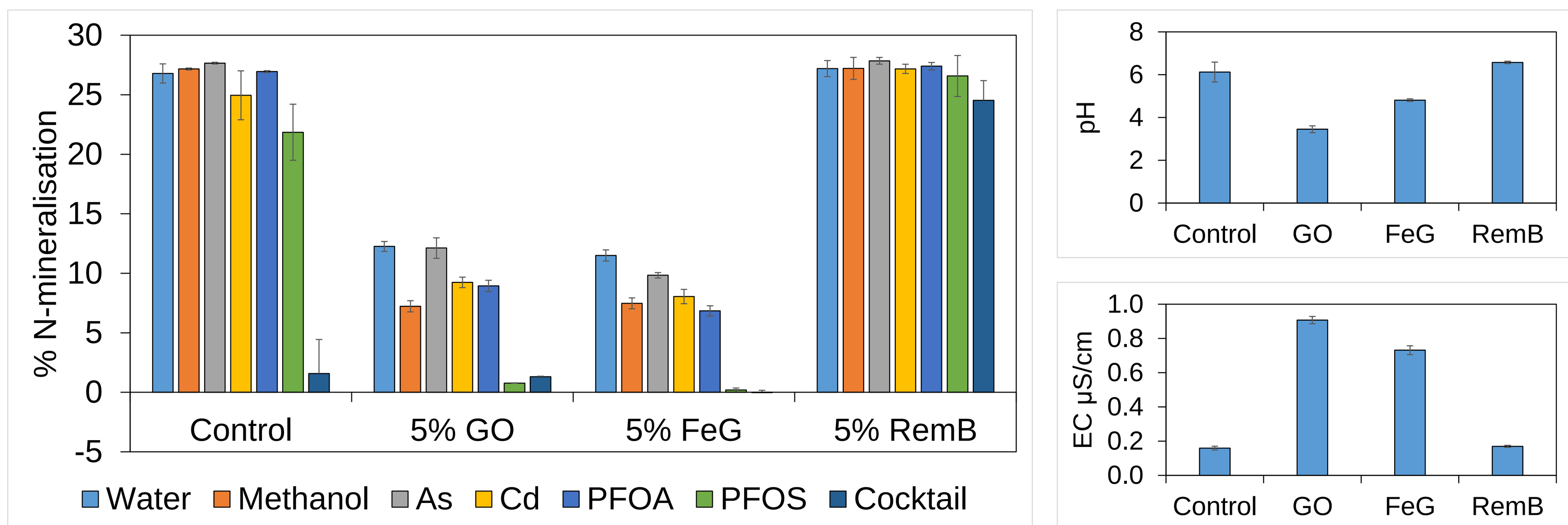
Impact of As, Cd, PFOA, PFOS on soil nitrification
Dose-response curves; 50% effect concentrations



Effect of remediation on contaminant bioavailability
As, PFOA, PFOS bioavailability ↓
Cd bioavailability ↑ in GBM-treated soils (low pH and high conductivity)



Effect of remediation on soil nitrification response
GO and FeG reduced soil nitrification
Low soil pH (~ pH 3.5 - 4) responsible



Summary

- As, PFOA ,PFOS bioavailability reduction by FeG and RemB (84 - 99%) >> GO (36 - 85%)
- Modification of GO with Fe-mineral phase enhanced performance
- FeG and RemB: mixed mineral + C-based sorbents; multiple binding mechanisms
- Binding sites not saturated
- Acidity of GBMs a challenge (impact soil nitrification function; impede immobilisation of cationic metals like Cd)
- Application *in situ* for soil remediation requires neutralisation of acidity

Contact: Supriya.Lath@adelaide.edu.au; Supriya.Lath@aecom.com (current affiliation)

References:
1. Marcano, D.C., et al., Improved Synthesis of Graphene Oxide. ACS Nano, 2010. 4(8).
2. Cong, H.-P., et al., Macroscopic Multifunctional Graphene-Based Hydrogels and Aerogels by a Metal Ion Induced Self-Assembly Process. ACS Nano, 2012. 6(3).

Acknowledgements:
We would like to thank Adelaide and Waite Microscopy for access to electron microscopy facilities. Financial support from ARC Discovery Grant DP150101760 is gratefully acknowledged. We would also like to thank Ziltek Pty. Ltd. for their financial support and provision of RemBind®.