The use of a hand-held mid-infrared spectrometer for the rapid prediction of total petroleum hydrocarbons in soil

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1. Background

TPH Background

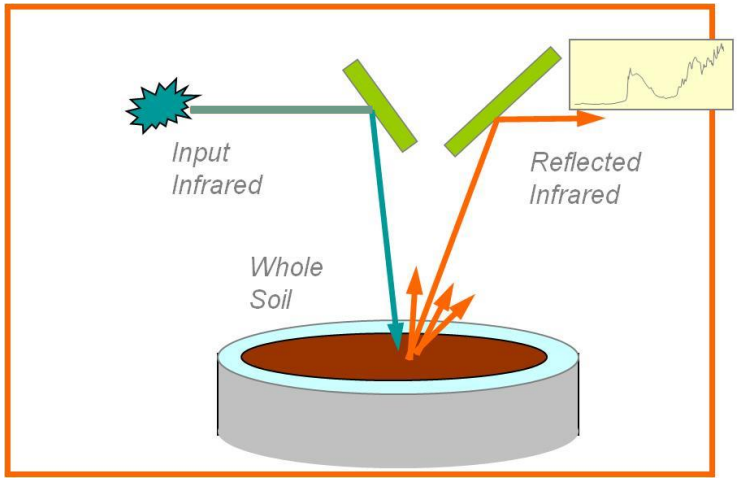
- Complex mixture of aliphatic hydrocarbon chains (C_{10}-C_{36}) derived from crude oil
- Major environmental pollutant: spills from production, storage and distribution
- Impacts: soil, sediment, water, biology and humans
- Risk assessment and remediation needs to be quick and is expensive

TPH traditional analysis

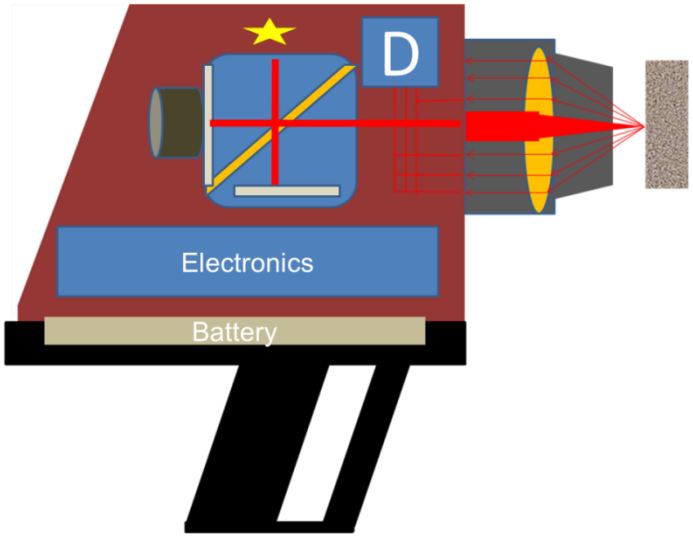
- Traditional approaches
  - Laboratory: Supercritical fluid extraction followed by silica clean-up and gas-chromatography with flame ionization detector (GC-FID)
  - Field: IR method (ATR) which requires extraction prior measurement
- We need a reliable, quick, cheap and “in situ” technique

DRIFT-PLSR as an alternative

- We propose diffuse reflectance mid-infrared spectroscopy together with partial least squares as an alternative for the “in situ” prediction of TPH (C_{10}-C_{36})
- Advantages
  - Rapid
  - No sample pretreatment
  - In situ
  - Multiple analytes prediction



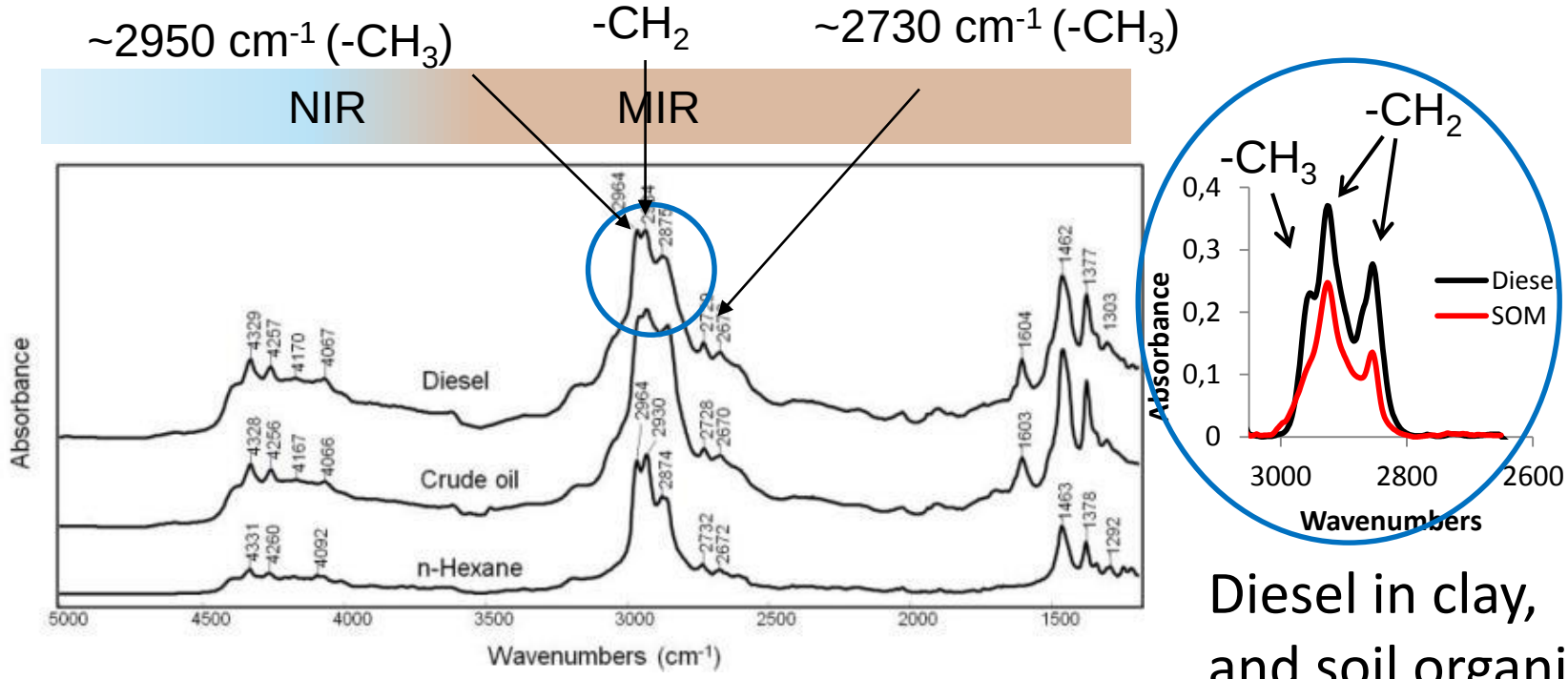
Our hand-held spectrometer



- Full FT-IR Hand-held (Agilent)
- 6000-650 cm^{-1}
- 15 s scan and 8 cm^{-1} resolution
- ~3 kg
- Blue-tooth PDA with PLS software
- Battery

TPH peaks

- Mid-infrared sensitive to C-H bonds



Diesel in clay, and soil organic matter spectra

NIR (5000-4000 cm^{-1}) and MIR (4000-1200 cm^{-1}) spectra of liquid diesel, crude oil and n-hexane

Forrester et al. 2013 (SSSAJ 77, 450-460)

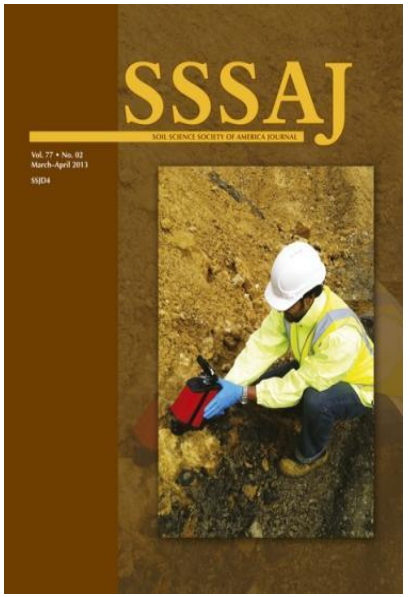
The PLSR model

- Selection of optimal spectral range and PLSR development in Forrester et al. 2013 (SSSAJ 77, 450-460)
- n = 199 TPH contaminated soils from Australia (0-15,000 mg/kg)
- Air-dried
- Partial least squares and trained by cross-validation

4540-4120				**3000-2600**			
PCs	R^2	RMSE	RPD	**PCs**	**R^2**	**RMSE**	**RPD**
9	0.84	853	2.4	**7**	**0.92**	**601**	**3.4**
(4330, 4260)				(2960, 2930, 2850, 2730)			

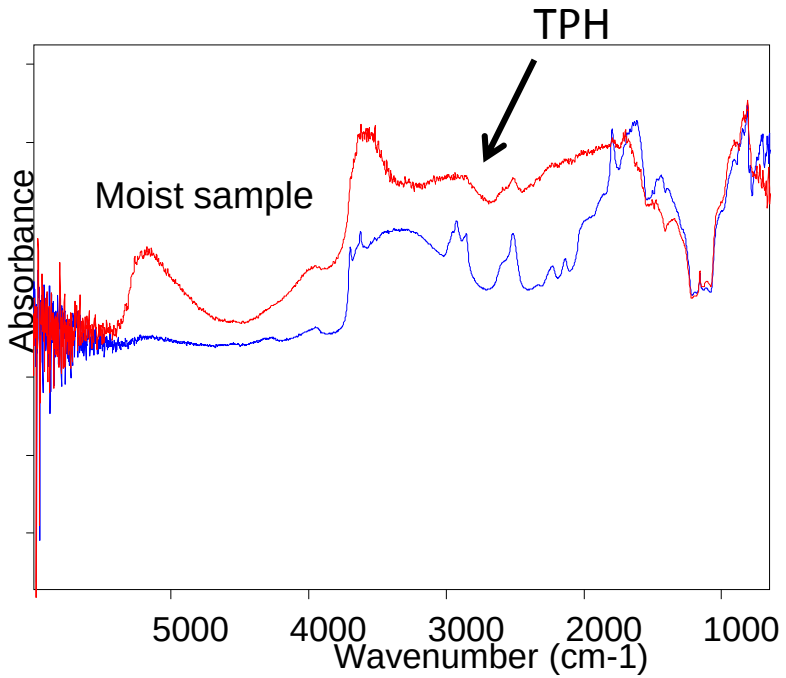
Commercialisation of the technique

- 2008-2009: collaboration project with Ziltek Pty Ltd (South Australia)
- 2012: Method patented in Australia
- 2013: method patented in USA
- 2013: Ziltek Pty Ltd. releases the technology as REMSCAN
- 2013: Publication in SSSAJ describing the patented method (Forrester et al., 2013)



Challenges

- Presence of moisture: leave the sample drying, software cut-off
- Soil heterogeneity: repeated scans, mixing the sample
- Sample entering into the cone nose: instrument squared to the surface and sample tamped flat



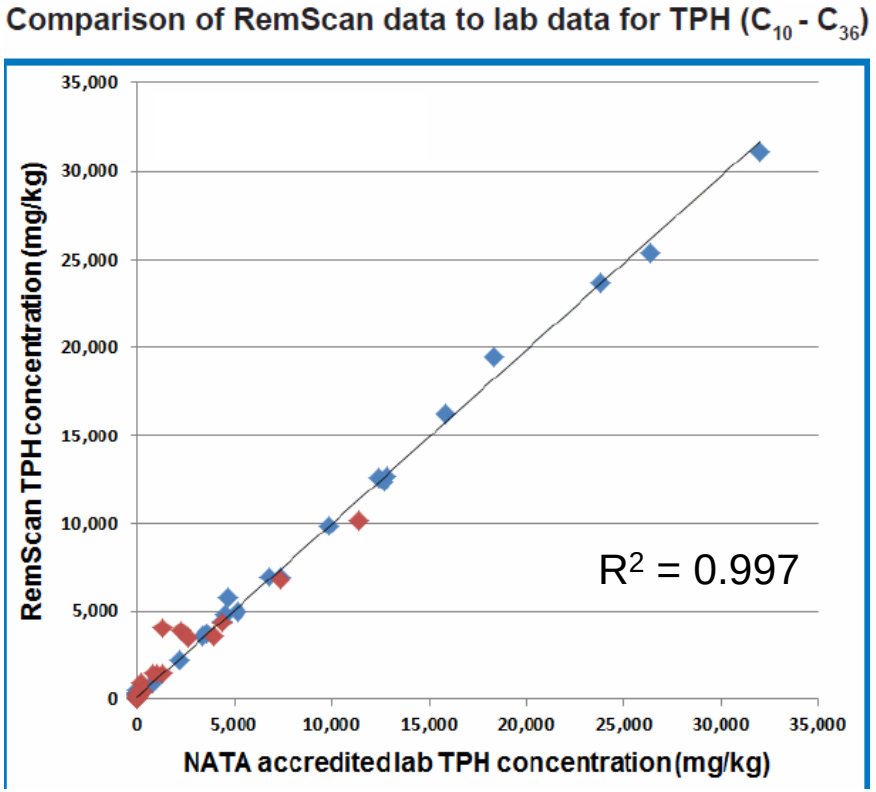
Challenges

- Soil type (TPH spread in sandy soils vs “shielding” effect in clay soils): site specific or local models. Local models:
  - Spectral library divided in clusters linked to textural classes
  - Unknown spectra allocated to the correspondent model
  - Within each model, 5 TPH range concentrations models: final model dependent on the TPH value predicted

2. Examples of field uses

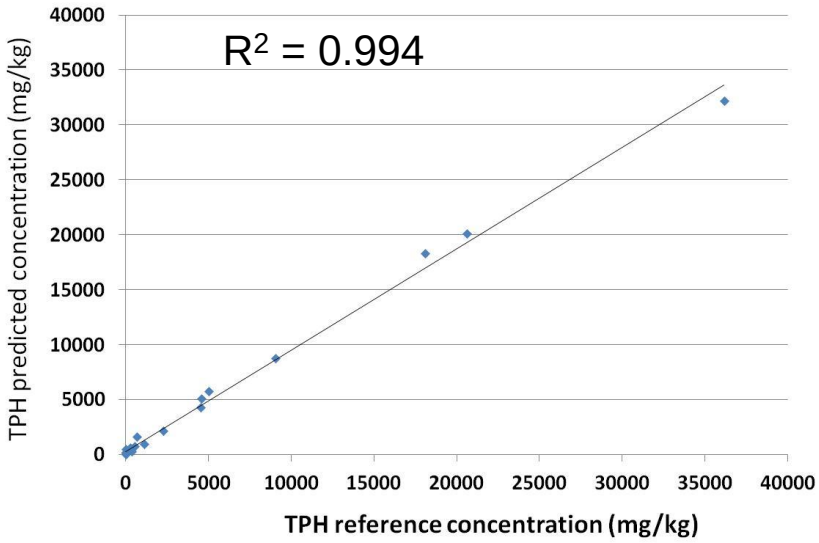
Case study 1: Western Australia

- Diesel leaked from a storage facility and captured in an emergency bund area
- Site specific calibration to quantify diesel in the bund area and monitor remediation works
- Remediation work completed in 4 days (200 samples/day)
- 19 ´blind´ samples sent for analysis



Case study 2: South Australia

- Ageing power transformer removed. Oil contamination in the footings
- RemScan "guided" the remediation work: pit declared "clean" < 1000 mg/kg



- Samples from from walls and floor sent to reference laboratory
- Reference analysis confirmed TPH predictions

Case study 3: South Australia

Final remarks

- DRIFT-PLSR using a hand-held spectrometer is suitable technique for the rapid, cheap and accurate prediction of TPH
- RemScan commercialy used
- On-going work
  - Inclusion of new soils in the global calibrations
  - Inclusion of additional contaminants

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