Analysis of Soil in the Field using portable FTIR

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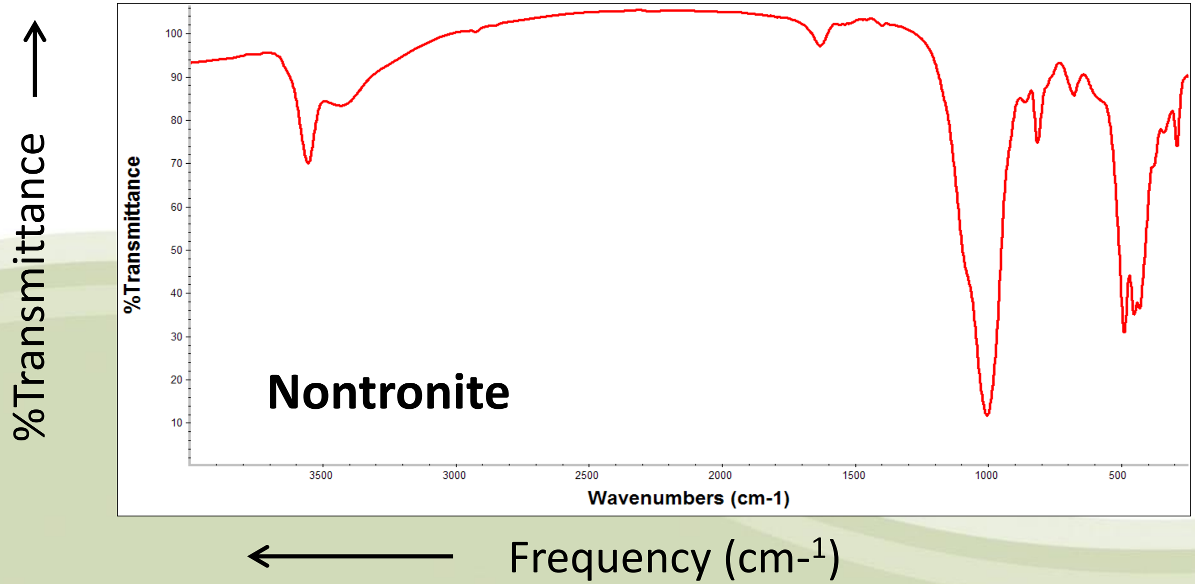
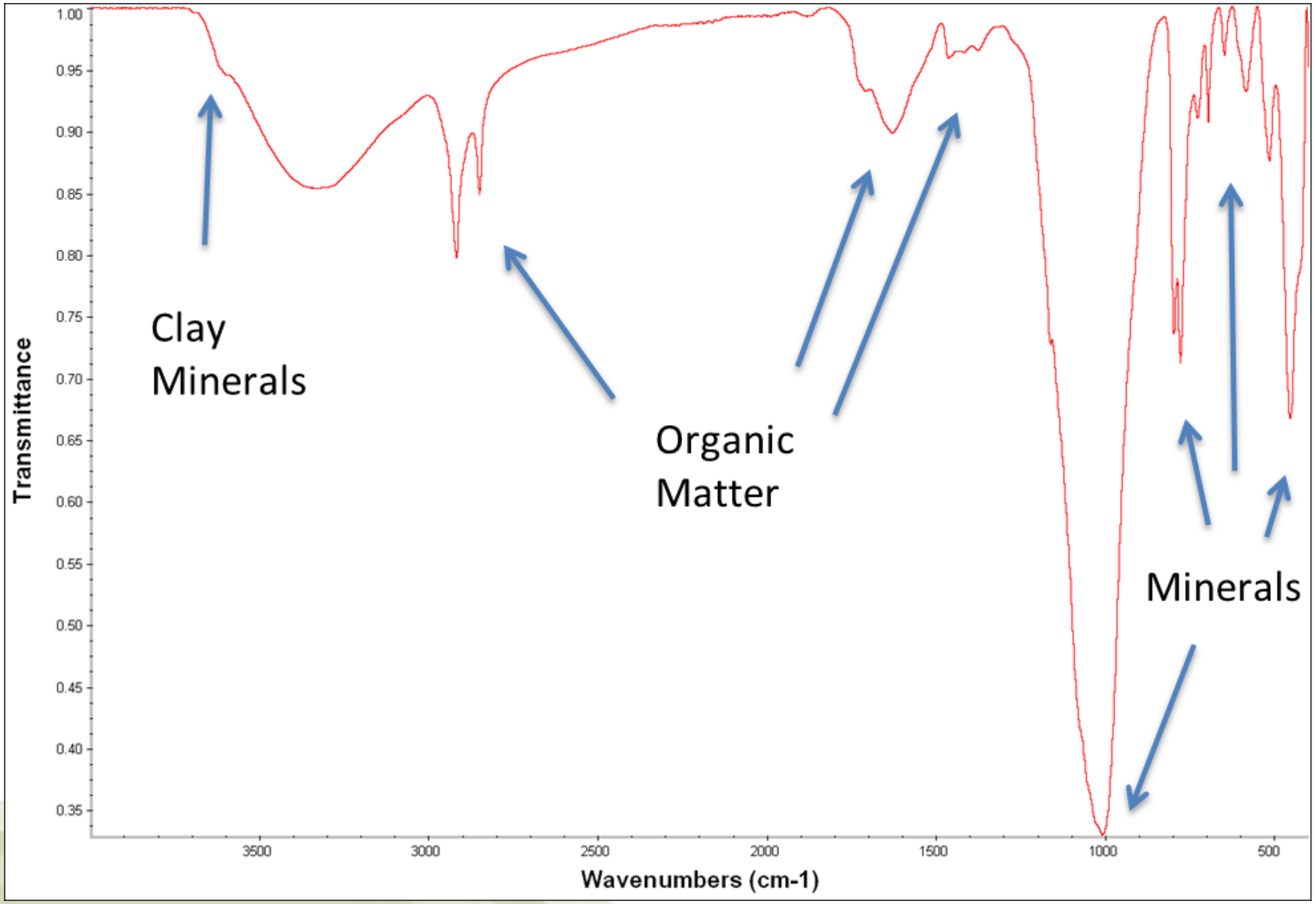
FTIR of Soil

- An FTIR (Fourier Transform Infrared) spectrum in the mid infrared (MIR) region, produced when infrared radiation is absorbed by a soil sample, gives the overall chemical profile of the soil
- Importantly, FTIR spectra can provide information about both the **organic** and **mineral** components of the soil
- Absorption bands in the IR spectrum (4000 to 400 cm^{-1}) relate to fundamental vibrations of the functional groups present in the sample

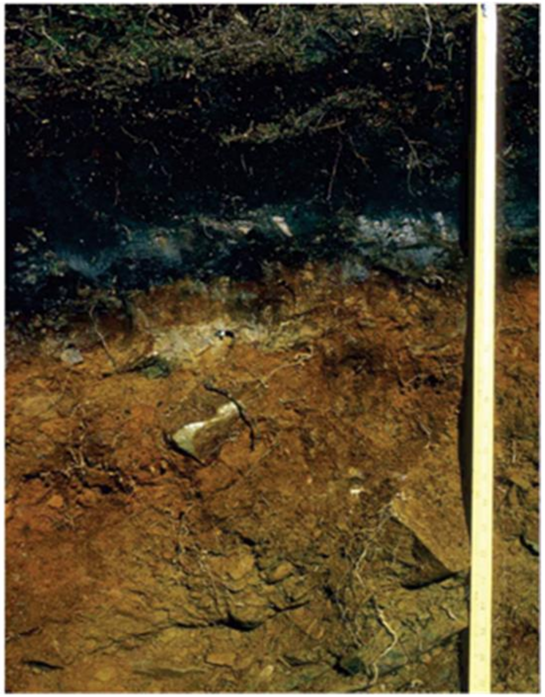


Interpretation of an FTIR spectrum of Soil

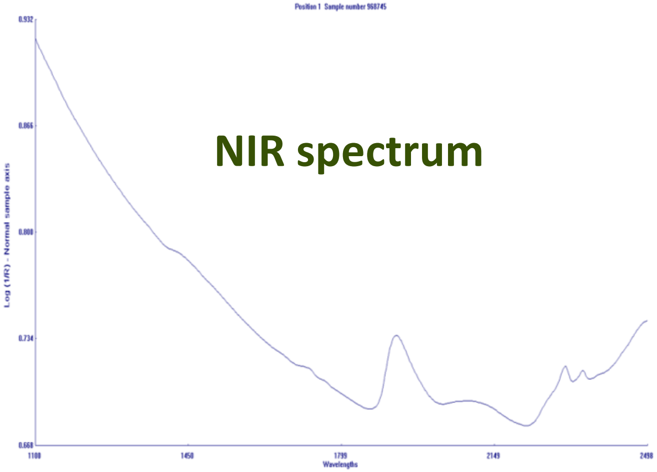


The IR spectrum of a soil sample can be readily interpreted to give information on the nature and proportions of the soil organic matter and the minerals present

FTIR or NIR for soil analysis?



Albic histic Podzol



NIR spectrum

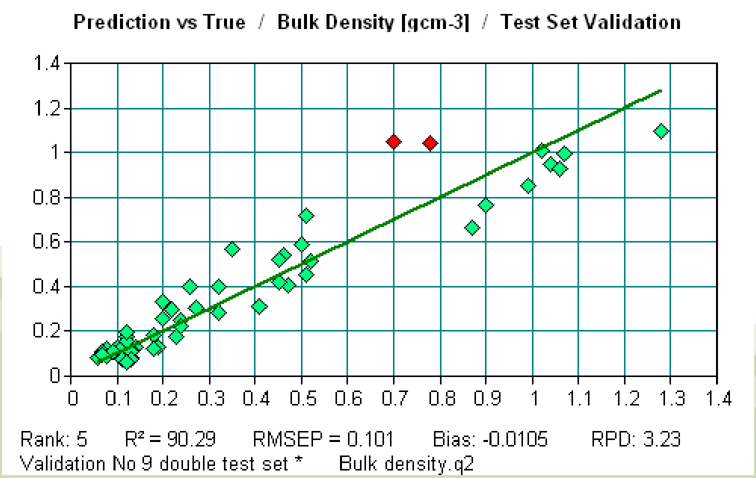
- To date, the NIR spectral range, with diffuse reflectance spectra, has been more widely developed than the FTIR technique using the MIR range
- It is seen as being cheaper and having technology that is more easily transferable to the field

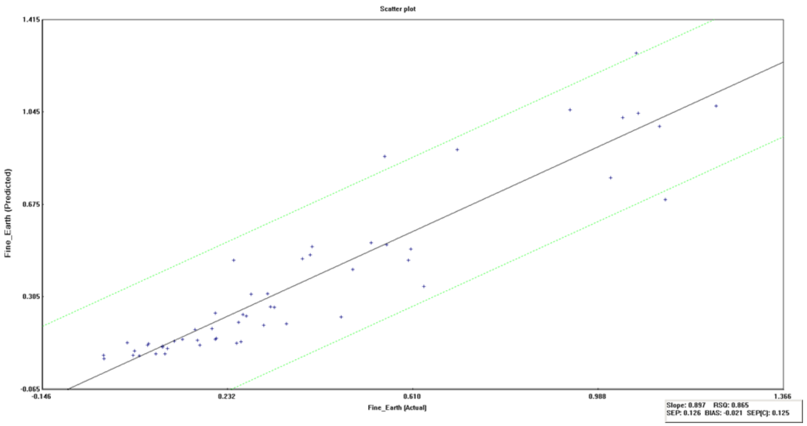
FTIR spectrum

Calibrations of IR spectra against soil properties

- Calibrations, developed by correlating the spectra to "wet chemistry" soil analyses, give the potential to predict a whole range of attributes of a soil from a single spectrum
- Calibrations have been developed for both NIR and FTIR spectra, including one for Soil Bulk Density (BD)

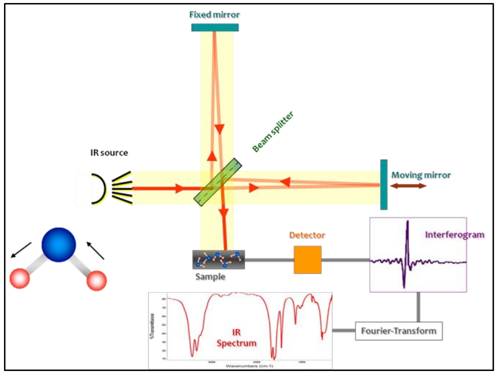
For the best FTIR BD equation developed, predicted versus actual results for an independent validation set of 55 soils had the following statistics:
R^2 = 0.903, SEP = 0.101, bias = -0.0105 and
RPD (SD/SEP) = 3.29





For the best NIR BD equation developed, predicted versus actual results for an independent validation set of 55 soils had the following statistics:
R^2 = 0.865, SEP = 0.126, bias = -0.021 and
RPD (SD/SEP) = 2.6

Portable FTIR



Schematic of an FTIR Spectrometer

Lab Based FTIR

All FTIR features incorporated into the ExoScan (Agilent), a handheld device

Portable FTIR

Moving FTIR Analysis into the Field

•The handheld FTIR allows *in situ* characterisation of samples

•No sample prep required

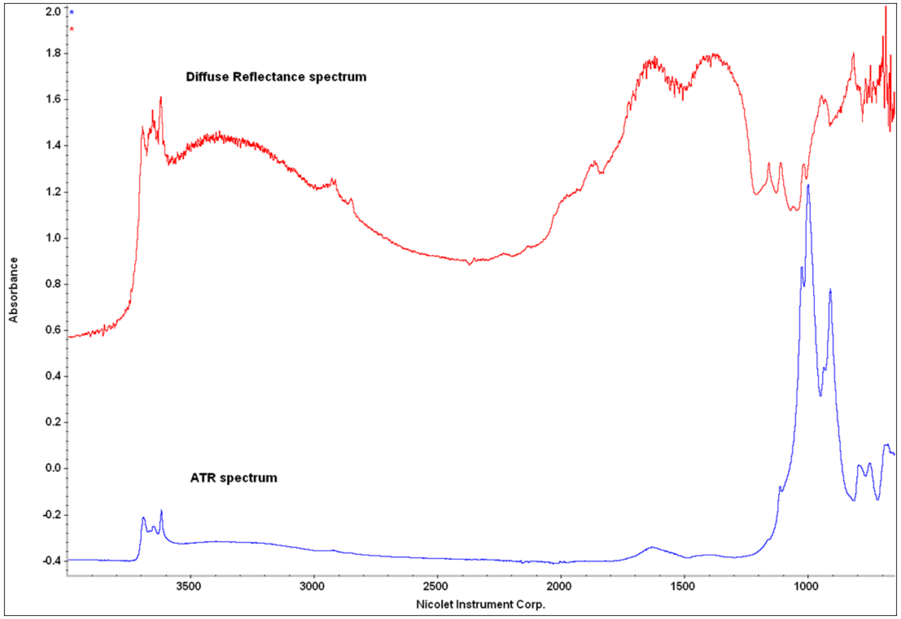
•Non destructive

•For soil analysis, however, problems created by variable soil moisture and variable particle size issues

•Heterogeneity and effective sampling always an issue with field based analysis (no milling)

Sampling options for FTIR in the field

- The FTIR spectra of soil samples can be recorded using a range of different sampling methods: Transmission; Diffuse Reflectance (DRIFTS) and Attenuated Total Reflectance (ATR)
- NIR is predominantly diffuse reflectance but not necessarily the best option in MIR region
- Both DRIFTS and ATR spectra can also be recorded in the field
- The Exoscan has changeable sampling head to allow both

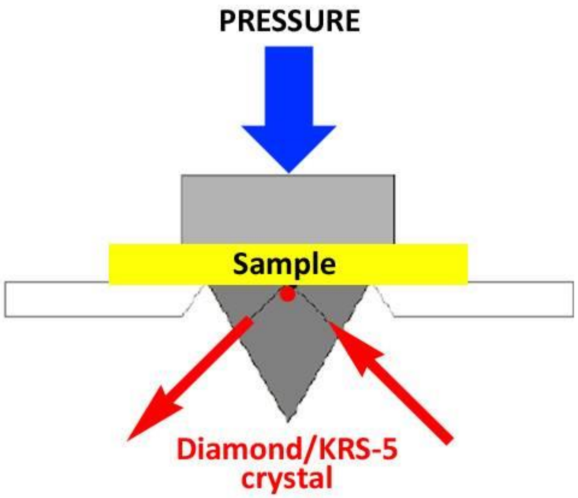


The spectra produced appear very different for the two techniques and assessment of which sampling strategy is most effective, for which soil parameters is important

DRIFTS spectra of soil

- Radiation is lower energy than NIR and penetrates less into the sample
- Can be noisy
- Diffuse reflectance of neat soil in the field produces spectra with inversion for strong absorptions, can be difficult to interpret (also will change with strength of different components)
- Possible to dilute the samples and avoid this problem – KBr in the lab but SiC paper an option in the field?
- Link to remote sensing data
- Advantage of enhanced overtones

ATR (Attenuated Total Reflectance)

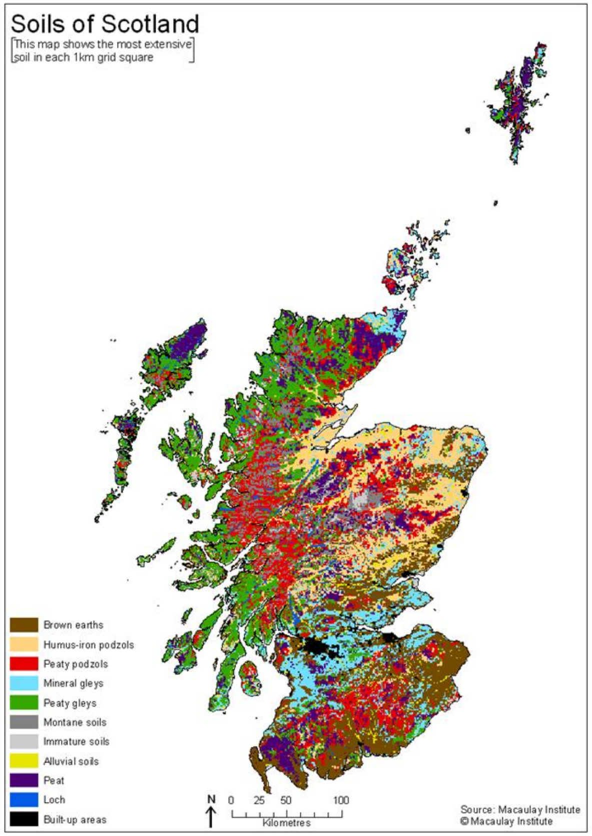


Schematic of a single bounce ATR

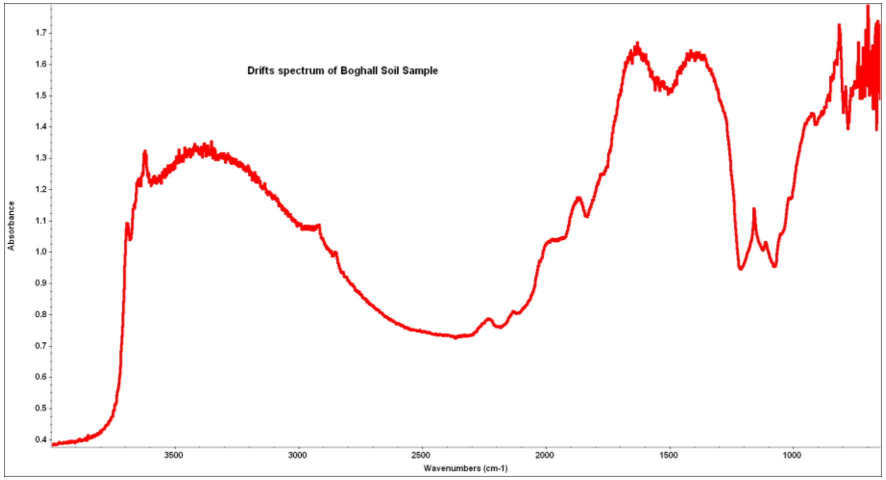
- **ATR "transmission like" and easy to interpret**
- **2 µ depth of penetration (variable with wavelength), no concentration issues**
- **Direct contact needed with diamond window – smear or field clamp both make easy sampling**
- **Better quality spectra?**
- **Un-milled spectra enhanced in OM and clay minerals which can be beneficial for calibrations**

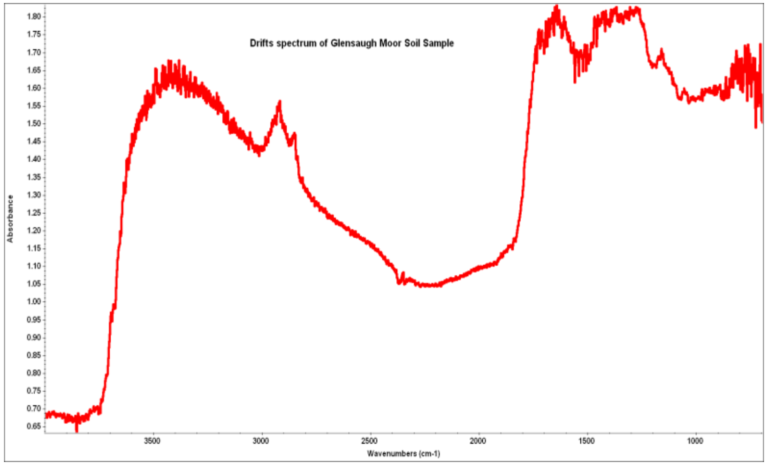
Test data set

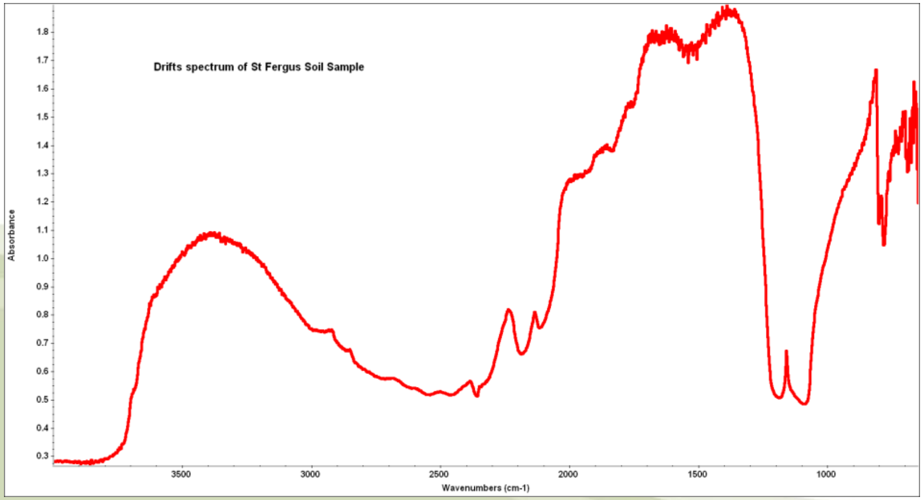
- Small test set of 20 soils from Scotland and Northern Ireland
- pH range from 3.3 to 7.1
- %C range from 0.6 to 27.5
- %N range from 0.01 to 1.0
- Varying geology



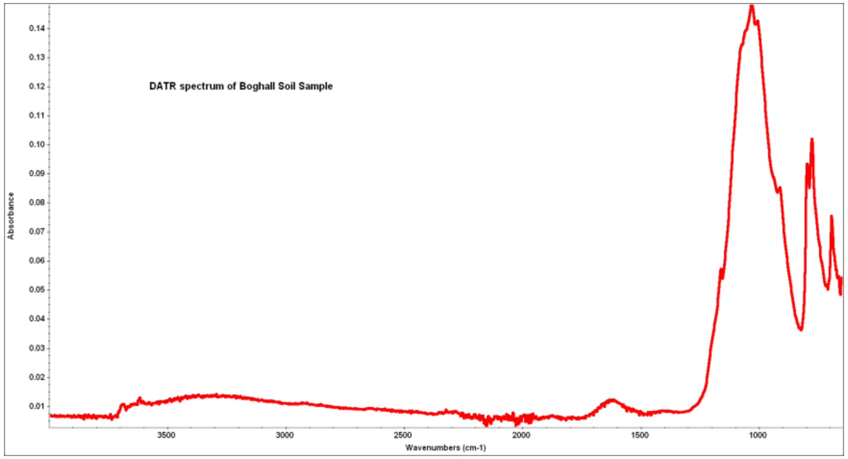
Drifts spectra (neat, dry, unmilled)

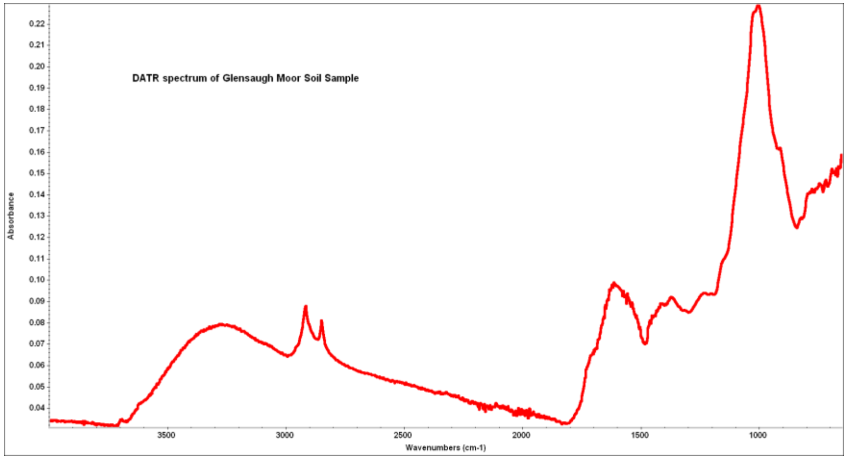


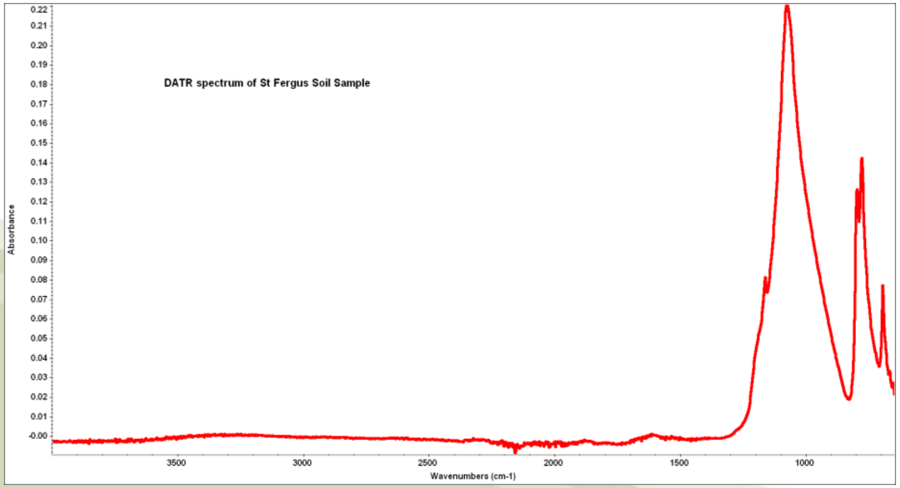




DATR spectra (neat, dry, unmilled)







Sampling "field condition" soil

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- In addition to the un-milled nature and variability of the soil moisture (particularly in Scotland!) becomes a problem
- This has to be dealt with either at the time of sampling or by processing afterwards
- Liquid water and water vapour can cause interference, but the effects of the water vapour are easier to subtract out

Comparison of “wet soil” ATR spectra

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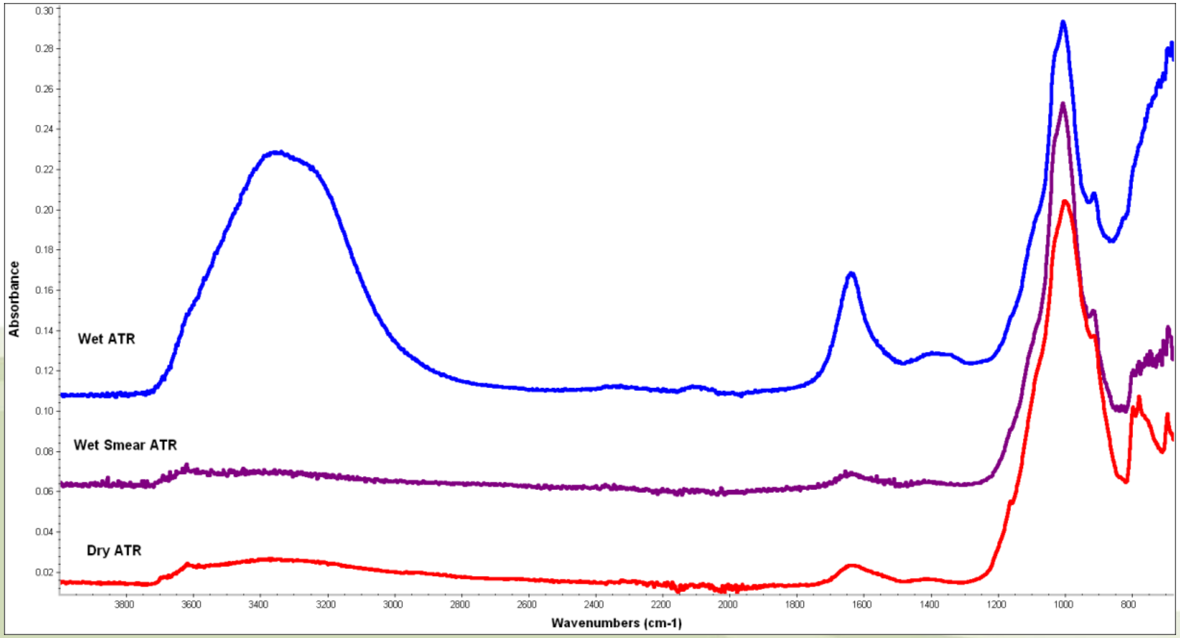
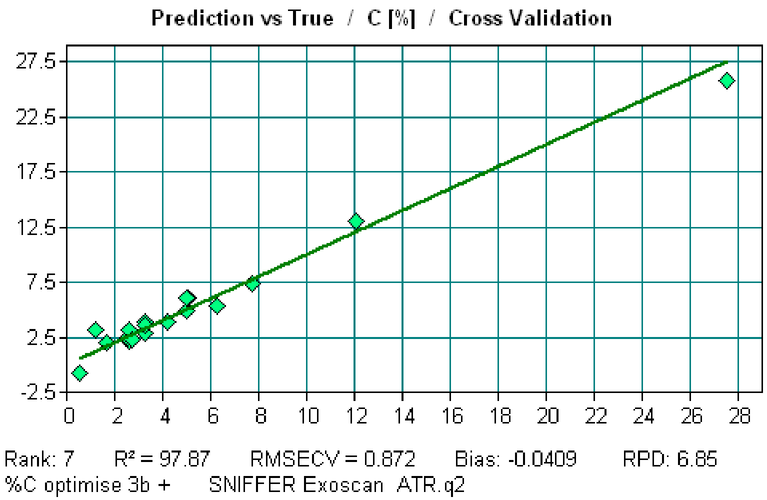
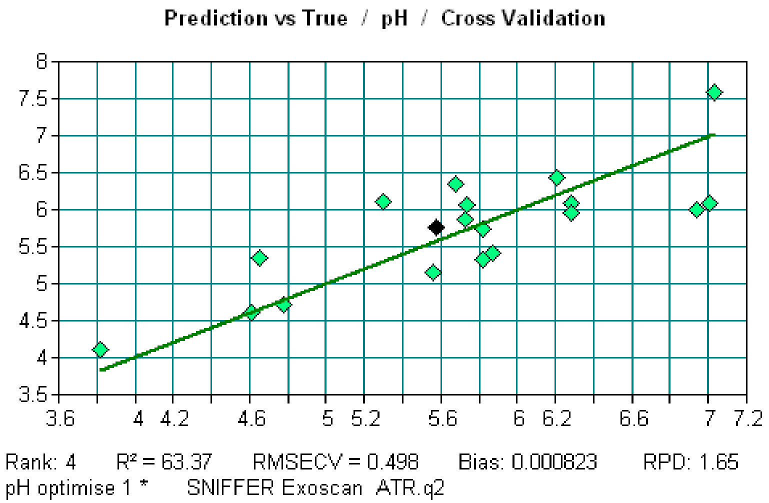
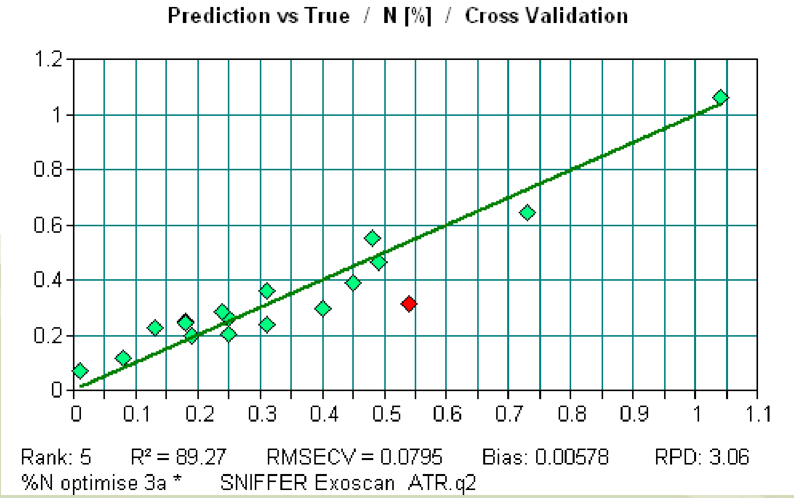
- ATR spectra were recorded of wet, field condition soil using the Exoscan
- Readily sampled by ATR as no pressure needed to get the required contact with the window
- Initially smeared using a spatula and allowed to dry
- Effective technique developed for using a gloved hand to produce a thin smear which dried very quickly, and closely resembled dry spectra



ATR calibration -dry milled

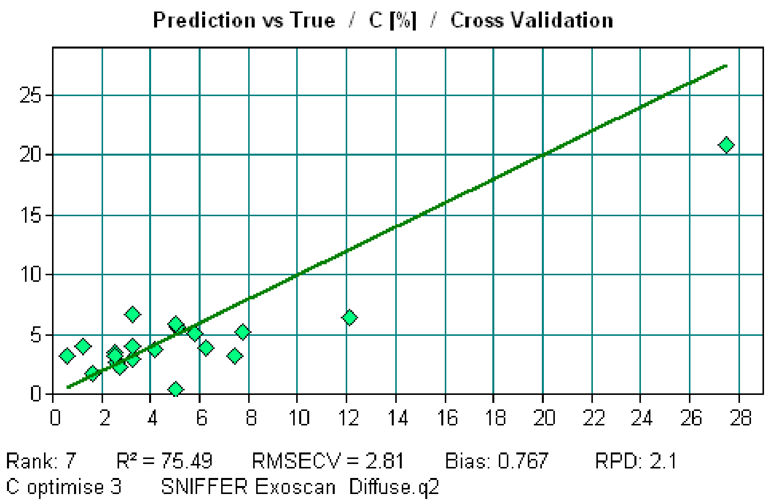






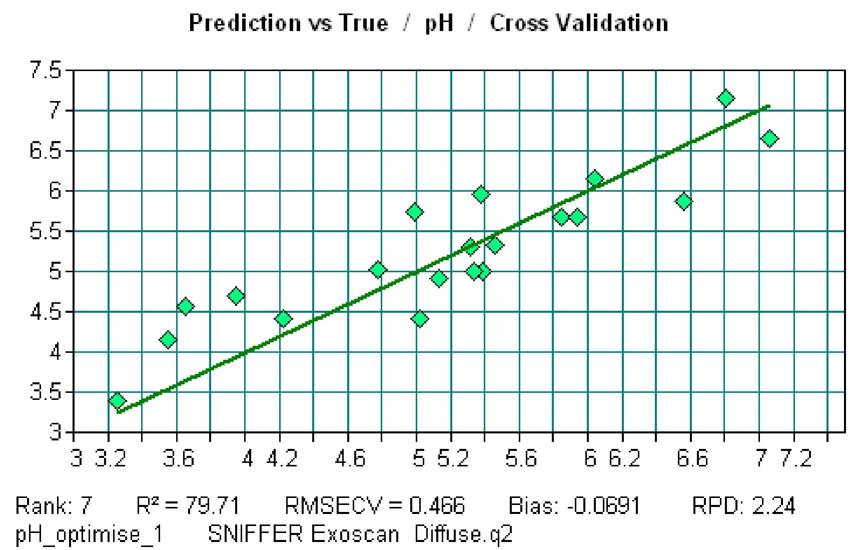
For the un-milled ATR calibration for %C :
R^2 = 96.5, RMSECV = 1.08
Bias = 0.0758 and RPD = 5.38

DRIFTS calibration -dry un-milled soil

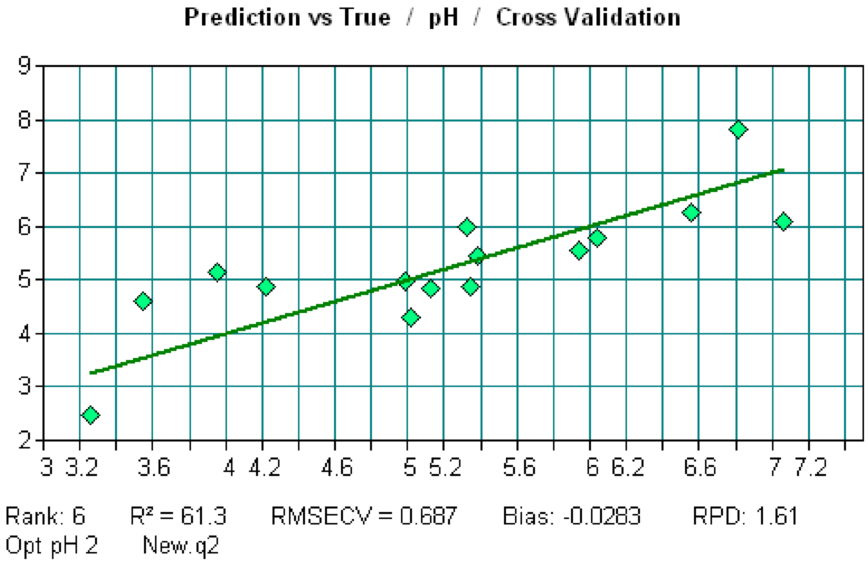


For %C the calibration for the DRIFTS spectra appears slightly poorer than for the ATR spectra

For pH the calibration for the DRIFTS spectra appears better than for even the ATR spectra of milled samples

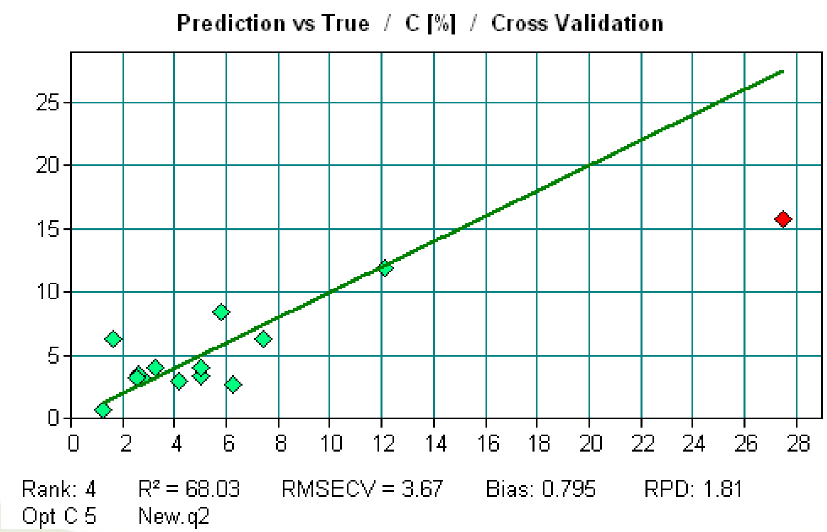


Wet un-milled ATR "smear" calibrations



For pH calibration for the "wet smear" spectra there isn't much deterioration from the calibrations for the ATR spectra of dry soil

For %C the calibration for the "wet smear" spectra is poorer than for the calibrations for the spectra of dry soil, but shows potential for development



Conclusions

Although this study has been carried out on a very small test set of soils, it gives some clear indications of potential and limitations for FTIR analysis of soil in the field

Consideration needs to be given to the different sampling methods possible and the conditions and parameters which they may be suited to

In this study, %C appears more accurately predicted by ATR spectra than DRIFTS, but pH is the reverse

By further developing a reliable method for putting a thin, quick drying smear of soil onto an ATR window it may be possible to avoid the problems resulting from moisture

Acknowledgements

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