



Discussion paper

Reply to “Comment on “Potential of integrated field spectroscopy and spatial analysis for enhanced assessment of soil contamination: A prospective review” by Horta et al”



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We thank Philippe C. Baveye and Magdeline Laba for their comment on our paper “Potential of integrated field spectroscopy and spatial analysis for enhanced assessment of soil contamination: A prospective review”.

From our careful reading of the comments provided, it seems that the main problems identified with our paper are:

- proposing the use of field Vis-NIR to detect organics and heavy metals in contaminated soils;
- proposing the fusion of Vis-NIR and PXRF spectra to estimate organics and heavy metals concentrations in contaminated soil.

According to Baveye and Laba:

- a) ... Vis-NIR cannot “see” these chemical elements in soils at all, unless their concentration is exceptionally high ($>4000 \text{ mg kg}^{-1}$).
- b) ... the only way Vis-NIR sensors can be used to quantify the concentration of soil-borne trace metals is via “surrogate” correlations ..., such correlations may exist in cases where high trace metal concentrations in soils are linked to the geology of the region, but in situations of recent accidental spills or other anthropogenic contamination, one cannot expect that the amount of trace metals have reached equilibrium with soils and therefore be correlated with any soil feature probed by Vis-NIR spectroscopy.

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- c) ... One issue that has not been mentioned much in the literature has to do with light penetration in soils. Since Vis-NIR relies on the interaction of light with soil materials, the layer of soil that it probes is very shallow surface... In addition, the first few millimeters of soil experience different (higher or lower) temperatures than deeper regions of the soil profile, and this may also, directly or indirectly, affect the fate of organic compounds. Therefore Vis-NIR measurements are more than likely poorly representative of what is happening in the bulk of the soils, unless these measurements are systematically carried out on freshly exposed soil surfaces.
- d) ... combination of potentially misleading Vis-NIR information with PXRF measurements is not likely to magically produce better results than what could be obtained via PXRF alone.

In response to comments a) and b):

The limitations associated with the use of infrared spectroscopy to detect and quantify heavy metals and organics in soils are fully acknowledged and commented in Sections 3.1 and 3.2 of our paper (Horta et al., 2015) (including the results of a laboratory experiments conducted specifically for this paper purpose).

However the possibility of considering Vis-NIR spectra appropriate to estimate contaminants in soils is confirmed in Sections 3.1.1 and 3.2 where we showcase published studies that successfully used infrared spectroscopy to detect and quantify heavy metals and organics in contaminated sites. From our analysis of published literature and our research experience with infrared spectroscopy, we concluded that:

- Many studies have shown that Vis-NIR can be used to predict heavy metal content in the soil. Infrared spectroscopy was usually able to predict total heavy metal concentration but not the extractable (or bio-available) concentration. The mechanism is normally attributed to adsorption of metals to organic matter, Fe/Al oxides and clay minerals. The abundance of the metals is indirectly correlated to these factors.
- There are conflicting results on the ability of Vis-NIR to predict certain metals. This indicates that the results or calibrations are site-specific.
- Vis-NIR spectroscopy should be able to readily predict organic contaminants due to the ability to detect chemical functional groups. However in soils, the spectra can be affected by soil

mineral interactions and organic matter, creating peak shifts and disappearance of the peaks compared to the pure absorption spectra of the contaminants.

- Challenges for infrared spectroscopy for hydrocarbon contaminants include evaluating the effect of volatilisation losses and degradation of the petrol compounds during sample collection and analytical process. Thus in situ measurements are recommended.

In response to c):

The limitations of using field infrared spectroscopy to analyse the entire soil profile were fully explored in Section 5 of our paper. We fully acknowledge that further work on calibration needs to be done to increase the accuracy of field infrared spectroscopy. Soil moisture undoubtedly poses a problem for soil property prediction in situ with both Vis-NIR and PXRF. It is also apparent that other in situ soil conditions can also reduce the accuracy of predictions. However chemometric methods that alleviate the influence of moisture and field conditions to NIR spectra have been developed and successfully tested in the field for soil organic carbon and clay content prediction (Ge et al., 2014; Ackerson et al., 2015). Further investigation is required specifically concerned with soil contaminants and how in situ soil conditions affect the predictive performance of Vis-NIR. Alternatively, one may compensate the less accurate in situ predictions with larger sampling intensities. The maxim that applies here is as follows: given spatial heterogeneity many moderately accurate predictions are equal to, or better than few, very accurate measurements.

In response to d):

It is our opinion that since both field Vis-NIR and PXRF produce estimates of a wide range of contaminants and these estimates are probably less precise than conventional laboratory-based assays, it seems prudent to combine the estimates produced from the two methods rather than favour one or the other. One analytical method may be more precise, for say heavy metals (PXRF), and the other for organic compounds (Vis-NIR). This however enhances the advantage of conjunctive use in the field – a wide range of potential contaminants can be detected at every site. The idea of gathering information from various sources seems to be one of the major propositions of chemometrics (Kowalski, 1975; Lavine, 2005).

Considering the field situation, we have the possibility of using both instruments (Vis-NIR and PXRF) on the same sample (volume of soil) within a small number of minutes. This is an example of field proximal soil sensing originally suggested by Viscarra Rossel and McBratney (1998), discussed in detail in Viscarra Rossel et al. (2010) and motivated by the need for high-resolution spatial and temporal soil information.

In conclusion,

We acknowledge the challenge of assessing the quality of Vis-IR and PXRF measurements to provide reliable estimates. Moreover, it is clear that work needs to be done to evaluate if these measurements should

be processed separately or combined to provide more accurate estimates. As researchers, we are motivated by these challenges and believe that they can be addressed appropriately to deliver a new and useful output to the industry of soil contamination assessment.

Finally, it is our opinion that our paper demonstrated the need to optimise current decision-based models for soil contamination assessment namely by improving the quality and quantity of information provided in the preliminary investigation stages.

Our review identified a number of key research priorities deemed necessary to ensure VIS-NIR and PXRF measurements can be used for soil contamination assessment. First, it suggests the design and construction of a soil contaminant inference system, where one can take measurements with the instruments in the field, in real time. Secondly, it highlights the need to investigate opportunities for data fusion (Wang et al., 2013) where data from all instrumentation are used together in order to make more accurate predictions.

Ultimately with the various soil spectroscopic instruments properly implemented, there is the potential to estimate a wide range of contaminants at one location with a known level of confidence – we can gain a great deal of information at a much reduced cost. Thus to optimise these new technologies, it is necessary to revise the current sampling strategy which is mainly based on grid sampling or stratified designs.

We believe that the approach presented in our paper addresses this current research gap and has the potential to be implemented as on-the-go field deployable software to provide a reliable and fast initial on-site contamination assessment. Given that we can estimate at any location the nature and degree of contamination it would be useful, indeed obligatory, to delineate areas of the site where remediation is required; one traditional way of doing that is to make a map.

Once again, we thank Philippe C. Baveye and Magdeline Laba for the comments which allowed us to further present and explain our work.

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