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Reflectance measurements of soils in the laboratory: Standards and protocols

Eyal Ben Dor [a,*], Cindy Ong [b], Ian C. Lau [b]

[a] *Tel Aviv University (TAU), Israel*
[b] *CSIRO, Perth, Western Australia, Australia*

ABSTRACT

For the past 20 years, soil reflectance measurement in the laboratory has been a common and extensively used procedure. Based on soil spectroscopy, a proxy strategy using a chemometrics approach has been developed for soils, along with massive construction of soil spectral libraries worldwide. Surprisingly however, there are no agreed-upon standards or protocols for reliable reflectance measurements in the laboratory and field. Consequently, almost every user reconstructs his or her own protocol based on the literature, experience, convenience and infrastructure. This yields significant problems for comparing and sharing soil spectral data between users, as spectral variations can be encountered from one protocol to the next. This further prevents the generation of a robust model for a given soil property using the worldwide data archive. To solve this problem in the laboratory, a joint project between CSIRO — Perth and Tel Aviv University (TAU) was conducted to establish a standard protocol for soil measurement, along with the use of an internal standard procedure to generate correction factors to normalize all possible variations to a soil benchmark (SBM) setup. The method is based on a proof of concept reported by Pimestein et al. (2011) for the use of an internal soil standard (ISS), a concept adopted from the wet chemistry discipline. To formulate the ISS method proposed herein, we used samples from two sand dunes that were characterized for their mineralogy, stability and reflectance reproducibility to be suitable for the standardization mission. These samples were found to be stable in space and time and to hold a stable soil structure and spectral response common to soils. Five soil samples were used to examine the performance of the suggested ISS approach. The ISS and soil samples were carefully measured for reflectance at the CSIRO laboratory using a new calibrated ASD and different protocols and procedures harboring minor and major differences. In addition, the exact same ISS and soil samples were measured in the TAU laboratory with a different ASD, protocols and ambient conditions. A systemic quantitative study was conducted to judge the performance of the ISS method. The results demonstrated that each protocol provides significant spectral variations from the SBM protocol, but all can be corrected to the SBM measurements. The results are promising as they can be achieved with any protocol if the systematic variations are kept constant. The ISS samples can also be used to track spectrometer deterioration and measurement-setup stability. The current paper provides information on how to obtain and use the ISS, and recommends a simple protocol for measuring soil reflectance under laboratory conditions.

1. Introduction

In the last decade, soil reflectance has become a well-recognized tool to assess soil attributes rapidly and accurately in the laboratory domain (Ben Dor, 2010). Soil proxies for many attributes, soil-mineral recognition and soil-type discrimination are the major applications that soil reflectance can contribute to soil practices. In recent years, it has been shown that soil reflectance can be used from both field and air domains using two major spectral technologies: portable point and airborne imaging spectrometry (Ben-Dor et al., 2009). With the rise in available portable spectrometers, more users in the soil discipline are entering the field and many soil spectral databases are being constructed in the laboratory to assist in other domains (i.e. http://www.isric.org/data/icrafisric-spectral-library).

Whereas spectral libraries of rocks and minerals have been quite popular over the past 30 years (Clark 1999; Crowley 1991; Crowley et al., 2003; Hunt 1977,1979,1980; Hunt and Salisbury, 1970,1971,1976; Hunt et al., 1971a,1971b,1971c; Gaffey 1985,1986; Swayze et al., 2007) and can be easily shared, for soils, despite the establishment of a few soil libraries, spectral sharing is quite limited. This is mainly because in rocks and minerals, mostly the absorption positions are important; in soils, for proxy models, not only are the absorption positions important, but also the intensity and shape of the spectrum are crucial. The first soil spectral library (SSL) was published by Baumgardner et al.

* Corresponding author.
E-mail addresses: bendor@post.tau.ac.il (E. Ben Dor), cindy.ong@csiro.au (C. Ong), Ian.Lau@csiro.au (I.C. Lau).

(1985), who collected hundreds of soil samples from the US and categorized them into five major soil types. Later, when soil proxy became a feasible method, it was understood that the SSL must be accompanied by chemical attributes of the soil samples (together with their spectra), and these two databases (spectral and chemical) were integral parts of the SSL (Shepherd and Walsh, 2002; Brown et al., 2006).

In the last 5 years, there has been a growing effort to generate more local SSLs by professional users who would then contribute and exchange their data internationally to form a world SSL archive (Viscarra Rossel, 2009). Generating SSLs in a large-scale domain is a growing and important mission that has recently been adopted by many organizations and entities, at both the national (e.g. Knadel et al., 2012) and continental (e.g. the LUCA SSL in Europe; Stevens et al, 2013) levels. It is predicted that there will be an increased in activity in this research as more SSLs are established and shared by the soil spectroscopy community.

To succeed with a soil proxy model, both chemical and spectral data have to be carefully acquired, to minimize the systematic and random effects. However, this is impossible when the population and measurement conditions (e.g. soil types, instrumentation and protocols) vary or are unknown (Brown, 2007). This problem generates significant constraints to obtaining a robust model for given attributes using "merged" SSL data, and blocks any attempts to compare them (Wetterlind and Stenberg, 2010). In contrast to chemical analyses, there are no agreed-upon protocols for soil spectral measurements. Users therefore prefer to keep their successful protocol active and are not open to examining others. One way to prevent possible systematic variations might be achieved mathematically, by following procedures such as spectral derivation or standard normal variate (SNV). However, in the case of high variations, these procedures could be problematic. A more basic method that deals with the physical parameters and spectral origin is thus needed.

To solve this problem, Pimstein et al. (2011) suggested adopting the idea of internal standards from the wet chemistry discipline for soils. Those authors demonstrated that well-known and agreed-upon reference material that is measured under any setup in any laboratory can be used to align one laboratory's spectral measurements to another's. They termed this material internal soil standard (ISS); their sample was not the ideal example to be shared throughout the soil spectral community; rather, it was useful as a proof of concept. Accordingly, the search for an ideal ISS remains active and the ISS idea cannot yet be implemented in SSLs worldwide.

This paper reports on a comprehensive study conducted to seek, identify and establish an ideal ISS sample and scale up Pimstein et al.'s concept for practical use. This is in order to create standards and protocols that will enable the comparison and use of every soil spectral measurement that has been acquired by different spectrometers, geometries and external conditions. The ISS sample was examined under minor and extreme conditions to check its suitability as a robust standard and to develop an agreed-upon spectral measurement for the soil spectroscopy community. This study involved a comprehensive collaboration between Tel Aviv University (TAU), Israel, and CSIRO — Perth, Western Australia.

2. Theoretical background

2.1. Factors affecting soil spectra

Two main factors can affect soil spectra: nonsystematic and systematic. The nonsystematic effects are those arising from uncontrollable phenomena, such as random noise and uncertain effects and instabilities (noise). To minimize the nonsystematic "noise" effects, it is important to maintain a consistent protocol. To achieve this, users must keep the instrumentation factors (instability of the spectrometer, illumination source, and detector output), as well as sample preparation, constant using an agreed-upon protocol. If these factors are not controlled, noisy and inconsistent soil spectra may result.

The systematic effects are those factors that arise from controlled responses that change from one instrument to the next but stay constant in a selected protocol. To prevent systematic effects, controllable and recordable factors such as the white reference (WR) sample, spectral configuration, measurement geometry, fore optic status, operator, particle size distribution and environmental conditions, are kept constant or tracked. If these factors are not controlled, the results may vary and hinder the ability to obtain good results from the chemometric analysis while using multisource SSLs; in practice, it may also prevent the sharing of SSLs between potential users.

Whereas the nonsystematic effects can be minimized by using an agreed-upon protocol, the systematic effects can vary from one laboratory to another. Consequently, a method to minimize the systematic effects is strongly required and effort in establishing measures to align different SSLs that have been generated using different protocols needs to be made. This issue is doubly important as such a method is lacking and cross-calibration between laboratory infrastructures is uncommon or nonexistent.

2.2. Description of the ISS principle and method

As previously discussed, the internal standard idea was adopted from the wet chemistry discipline to minimize systematic effects, where an agreed-upon and well-known (species and concentration) material is used to align the readings of any method (Willis, 1972). The internal standard idea is based on the fact that the nonsystematic effects are minimized by the protocol used in the professional laboratory, while the different systematic effects between protocols are corrected for using the alignment factor generated from the standard's reading. In general, an ideal ISS should be inexpensive, simple to use, easily delivered overseas, homogeneous, stable in space and time, and useful for both radiometric and spectral calibration. Pimstein et al. (2011) concluded that the internal standard also has to be as similar as possible to soil grain size (shape, size and nature) and if possible, it should have stable (and preferably chemically featureless) spectral performance across the entire spectral region. They indicated that their sand dune sample (90% quartz), which underwent a bleaching process with HCl and the DCB method (Mehra and Jackson, 1960) to remove calcite and free iron oxides, respectively, and was characterized by an average grain size fraction of <2 mm, is the preferred ISS sample. It was shown that other materials (flat polyethylene surface and glass crushed to <2 mm) cannot perform the correction as effectively as the sand sample and concluded, as previously mentioned, that the ISS must have "soil characteristics" in terms of shape and nature. Nonetheless, based on their proof of concept, they strongly recommended finding a better ISS sample from natural sources that satisfies their previous suggestions and does not need to be subjected to chemical processes. They also pointed out that such a sample must be tested, and be easy to disseminate to the scientific community at low (or no) cost with long-term availability to all.

3. Material and methods

3.1. ISS and soil samples

3.1.1. Internal soil standard (ISS)

We devoted an international effort to locate the ideal ISS samples that would satisfy Pimstein et al.'s (2011) criteria. Recently, in Australia, two sites were characterized as bright, homogeneous sand dunes (Fig. 1). They were found along the coastline of Wylie Bay (WB) and Lucky Bay (LB) in southwestern Australia. The sand dunes were sampled by collecting the top 10 mm (about 50 kg each) and brought to the laboratory to be further inspected for their fulfillment of ISS criteria. In WB 2 (33°49′ 23.89″S 121°59′51.81) the sand was sampled on a moderate slope of a 30-m high dune hill (under dry conditions), and in LB (33°59′ 17.22″S 122°13′51.89″), it was sampled at the waterfront (wet conditions). After arrival at the laboratory (2 days after sampling), the sand
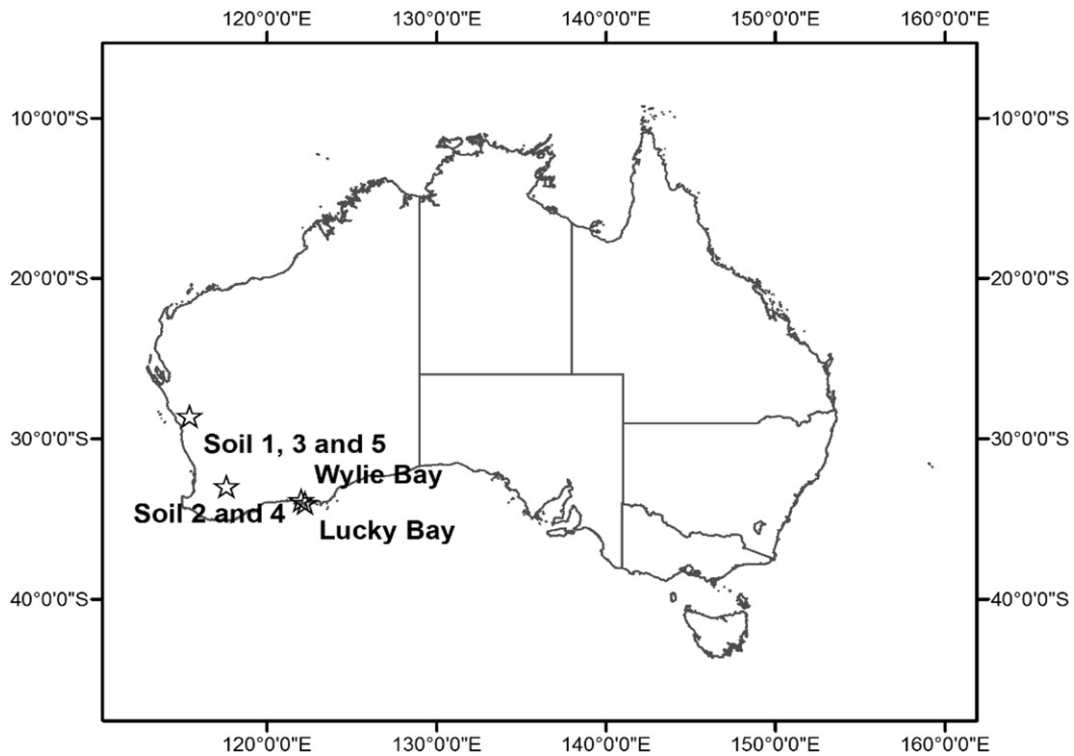
Fig. 1. The location of the two internal soil standard (ISS) samples selected for this study.

samples were immediately washed with distilled water several times until the EC of the leached water was low. The sand was spread out on a metal tray coated with filter paper and left in the oven for 48 h at 110 °C. After drying, the samples were cooled down to room temperature for 2 days and sieved to <500 μm for WB and <250 μm for LB (for the latter, two batches were prepared). In the LB samples, a thin (dark) crust evolved after heating which was gently removed before sieving. Samples were exposed to ambient conditions in the laboratory for 1 week, until equilibrium was reached, and moisture content that was measured by gravimetric method showed stability. Additional measurements (X-ray diffraction, differential thermal analysis (DTA),

thermal gravimetric analysis (TGA); Fourier transform infra red spectroscopy (FTIR) and particle-size distribution) were conducted to characterize the sand samples.

3.1.2. Soil samples

Five soil samples from Western Australia were obtained from sites at Mullewa, Toolibin and Buntine-Marchagee. All soils were air-dried and sieved to pass a 2-mm sieve and then stored in a 100 ml plastic container. Soil analyses have been determined as indicated in Table's 3 comment.
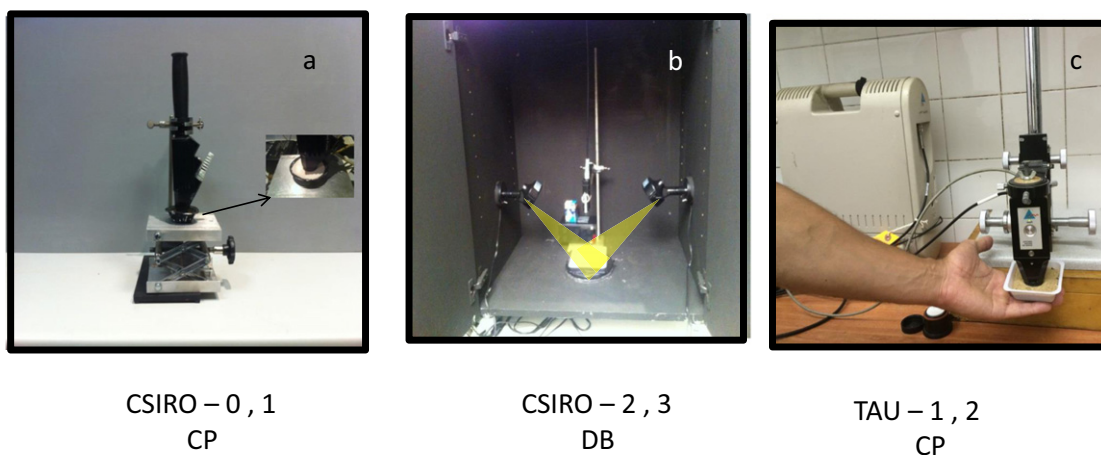

CSIRO – 0 , 1
CP

CSIRO – 2 , 3
DB

TAU – 1 , 2
CP

Fig. 2. The three measurement setups used to measure the soil reflectance. (a) The samples were lifted up to the CP assembly by manual elevator. (b) A dark box with fixed geometry was used. (c) The samples were held by hand to face the sapphire window of the CP assembly.

Table 1
The stability results of the cross examination between three ASD spectrometers and 4 contact probe assemblies at CSIRO (measurements were acquired over one week). All contact probes were model number A122300.

ASD/CP	1 (SN:00150)	2 (SN:00170)	3 (SN:644)	4 (SN:317)
1 (SN:6351)	++	++++	++	+++
2 (SN:6232)	++	++++	++	+++
3 (SN:16446)	++	++++	++	+++

++ bad (>5%) , +++ favorable (3-5%) and ++++ good (<3%).

3.2. Reflectance measurements

3.2.1. Instruments

Four ASD spectrometers (two ASD FieldSpec Pro FR SN:6232 and 6351 and a ASD FieldSpec3 SN:16446) and five different contact-probe (CP) assemblies were used in this study at two geographical locations: three spectrometers in the southern hemisphere at CSIRO (Perth, Western Australia) and one in the northern hemisphere at TAU (Tel Aviv, Israel). The spectrometers were used in the laboratories under the same ambient conditions: 22 °C and 12% RH at CSIRO and 26 °C and 40% RH in Tel Aviv.

In general, four basic geometric options were possible for the soil-measurement protocol: 1) use of a CP that touches the surface of the sample, 2) use of a bare fiber with a set viewing and illumination geometry (no contact with the sample) in a dark box (DB) environment, 3) use of an integrating sphere that collects radiation from all directions, and 4) measuring the reflectance through a glass petri dish (e.g. using the MagLight® from ASD). Only the first two options meet the conditions for a well-accepted protocol for most users worldwide. Although highly recommended, option 3 is not applicable in practice as the integrating sphere assembly is expensive and most laboratories do not have it. The fourth option, although easy to perform, suffers from nonhomogeneity of the petri dish glass' transparency, which adds another unknown factor to the spectral variation which cannot always be corrected for. Accordingly, the CP and DB options were selected to carry out the spectral measurements in this study. Both options were used at CSIRO, whereas only the CP option was used at TAU.

3.2.2. A short description of each measurement method used

The CP, DB at CSIRO: Both arrangements required 60 min warming up of the spectrometer and 30 min for the lamps. In the CP method, the sample was prepared by pressing the soil surface against a glass surface and bringing the bare sample to the CP by a stable elevator while the CP was held firmly in place (Fig. 2a). The measurements were carried out in a dark environment. In the DB method, a dark box with a constant geometry was set up (Fig. 2b), consisting of two 12 V and 35 W tungsten halogen lamps that illuminated the sample at 45°. A bare fiber was set up to measure from the nadir position, covering a field of view (FOV) of 100 mm diameter of the sample surface. The

measurements were done under two constant distances of the sample to the fore optic (10 and 13 cm). The sample preparation was done using a large sample holder (i.e. bigger than the FOV; a "cock dish") with surface preparation consisting of using a flat sheet of glass to apply pressure and flatten the surface. In both CP and DB methods some modification to the sampling method was performed to demonstrate possible systematic variations that could occur in reality. These consisted of differences in: geometry (CP and DB), white reference (both material and distances from the fore optics), sample holder geometry, sample preparation and distance from the fore optics (see later description). After each measurement, a check was performed to determine if the white reference (WR) was observed to have returned to 100%. If necessary the WR was retaken to set it back again to 100%. After every 2 soil samples (8–6 replications) the ISS was measured using the same configuration.

The CP at the TAU: Only the CP method was performed at the TAU, with 15 min warm up for both spectrometer and globe of the contact probe. The soil sample was prepared on a black plastic dish holding enough sample to cover 20 mm depth. The surface of the sample was smoothed with a stainless steel knife. A manual elevator was used to bring the contact probe to the sample, which held it stable during measurement (opposite to the CSIRO CP method) (Fig. 2c). Modifications were employed to the experiments at the TAU to demonstrate effects of systematic drifts, which included: differing the white reference (using a dirty surface); and using two different operators (an experienced user and an un-trained student). After every soil sample measurement and before each set (3–4 replications), the ISS was measured using the same configuration. After each of the 4 replicates of the soil sample measurements, the WR was checked to determine if it had deviated from 100%. If necessary, the WR was retaken to set it to 100%. In all of the protocols above, 3 to 4 replicates were measured for each of the two ISS samples. A replicate measurement of each of the samples was collected by stirring and re-preparing the sample holder before measurement. The reflectance variation observed at 1.6 μm between replicates of a given sample was <3% using the two methods tested at CSIRO and <6% at TAU. The variation between CSIRO and TAU might be a result of different conditions, such as the human factor, and stability of the instrument.

3.3. Selecting the soil benchmark spectral measurement protocol

The soil benchmark (SBM) is a spectral measurement of the ISS sample under agreed-upon standard conditions to which all other measurements are then aligned. For that purpose we examined at CSIRO the most stable ASD spectrometer and CP assembly from the inventory (3 ASDs and 4 CPs). The selection was based on checking the stabilization of each ASD-CP combination. The examination took place during a week where the same 99% reflectance standard and the WB-1 sample were repeatedly measured. Stability was judged based on the variation of the WB-1 reflectance output in each configuration as gathered over the week. The configuration that provided <3% variation in five

Table 2
The measurement set-ups with the modifications conducted at both CSIRO and at the TAU laboratories for carrying out the measurement of the same 5 soil samples and ISS sand samples.

Set-up name	ASD	CP	DB	WR-PTFE	WR-BaSO4	Operator	Distance	Method	Protocol	Sample holder	Status (relative to CSIRO 0)
TAU 1	(1*)	(1*)		Dirty	–	2	Contact	CP	3	A polyethylene cup	Major modification
TAU 2	(1*)	(1*)		–	Clean	3	Contact	CP	3		Sever modification
CSIRO 0	(2)	(2)		Brand new – a (clean)	–	1	Contact	CP	1	BLD	Soil benchmark method
CSIRO 1	(2)	(2)		CAP – c (clean)	–	1	Contact	CP	#1	BLD	Minor modification
CSIRO 2	(2)		(1)	Brand new – b (clean)	–	1	10 cm	DB	2	A paper black dish	Moderate modification
CSIRO 3	(2)		(1)	Brand new – b (clean)	–	1	13 cm	DB	#2	A glass dish	Moderate modification

DB — dark box, CP — contact probe.
Brand new — a = a clean 50.8 mm polytetrafluoroethylene 99% reflectance standard (LabSphere).
CAP — c = a clean (used) polytetrafluoroethylene cap that fits the CP sapphire window.
Brand new — b = a clean 85 mm polytetrafluoroethylene disc.
ASD — Analytical Spectral Device®.
BLD — a silver painted black "cake" dish.
Protocols: 3 (TAU), 2 (CSIRO dark box), 1 (CSIRO contact probe).

Fig. 3. The soil samples (a) and the internal soil standard (ISS) samples (b) used in this study.

measurements (1 per day) was then selected as the SBM setup. As seen in Table 1, the critical factor was the CP, and not the ASD instrument. Therefore, we selected ASD-2 and CP-2 for the SBM setup. It should be pointed out, however, that it is not important which setup is selected for the SBM alignment as long as it is stable and agreed-upon by the entire community. If a new SBM setup is to be selected, then a simple alignment between the current SBM measurements (ASD-2, CP-2) can be performed using the suggested ISS samples.

3.4. Modification from the basic protocols

In order to check the ISS performance and its potential we applied several staged modifications to each of the basic setups. There were minor to extreme changes to span all possibilities. The summary of these modifications is given in Table 2, along with a short description of each in the afterward section.

3.4.1. Explanation to Table 2

At CSIRO the CP method was used with two setups (CSIRO 0 and 1). CSIRO-0 was selected as the SBM setup (using ASD-2 and CP-2). This used a brand new polytetrafluoroethylene (PTFE) 50.8 mm disc (LabSphere SRS-99-020 AS-01161-060) as the WR which was held against the CP sapphire glass window during both optimization of the

Fig. 4. The spectra of the internal soil standard (ISS) samples (LB — a, WB — b) as measured by the CSIRO-0 setup.

spectrometer and WR measurement. The method for CSIRO-1 (ASD-2, CP-2) used a clean (used) 25 mm polytetrafluoroethylene cap, that fits exactly to the CP sapphire window (CAP-c). This WR was used during both optimization and WR calibration. Additionally at CSIRO, two additional setups were used with the DB configuration: (CSIRO 2 and CSIRO 3, with ASD2 and bare fiber) CSIRO 2 involved the maintaining of a distance of 100 mm from the fore optic to the sample in the dark box (DB) configuration (see Fig. 2b). The sample holder was a matt-black painted cardboard dish, 80 × 150 mm in size and 40 mm depth. The CSIRO-3 method maintained a 140 mm gap from the fore optic to the sample under the same DB lighting configuration. The sample holder was a glass dish 60 mm in diameter and 20 deep. In both of the above DB setups (CSIRO 2, 3), the same brand new PTFE disc of 50.8 mm in diameter was used. The PTFE disc was provided from a commercial supplier with a reflectance calibration between 250 and 2500 nm. At the TAU a different protocol from CSIRO was applied using a different ASD spectrometer and CP assembly (see the previous description). The procedure differed by moving the CP assembly toward the sample (opposite to CSIRO-CP setups where the sample brought to the CP; see Fig. 2c). Also, at the TAU the spectrometer was warmed up for only to 15 min before the measurement was started. In the TAU-1 a dirty PTFE disc was used as the WR, whereas in TAU-2 packed BaSO$_4$ powder was used as the WR. Different users were used at the TAU to conduct the measurements, one per each setup (TAU-1 and TAU-2) and different room conditions were encountered relative to those at CSIRO. The following summarizes the difference between TAU and CSIRO setups: 1) different spectrometers and calibration dates, 2) different CP and geometry (CP against DB), 3) different warming up conditions, 4) different room conditions, 5) different measurement protocols, 6) different white reference (WR) and 7) different operators. In both locations the same exact samples (either soil or ISS) were measured.

3.5. Spectral correction to the soil benchmark (SBM) measurements

As Pimstein et al. (2011) suggested, an agreed-upon ISS sample and setup, composed of "benchmark spectra" (SBM), have to be used for correcting the other setups. As previously discussed, the CSIRO-0 setup was selected as the SBM configuration, where both WB and LB were used as the ISS samples. The two samples represent independent replicates for the ISS correction as described above. The measurement
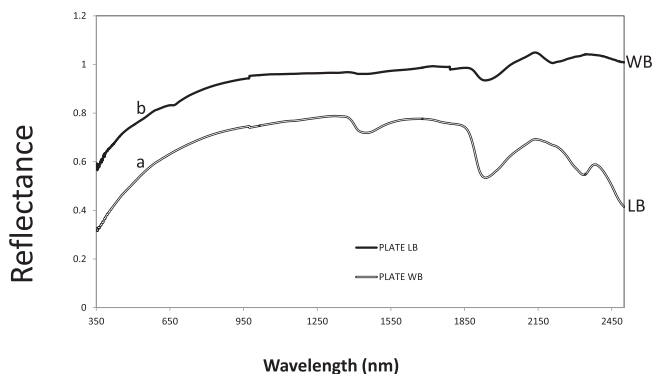
Table 3
Basic characteristics of the five soils used to examine the ISS concept, using WB and LB as ISS samples.

	CSIRO code	Site name	Laboratory name	Clay (%)	Silt (%)	Sand fine (%)	Sand coarse (%)	Organic carbon (%)	CaCO₃ (%)	DPTA iron (mg/kg)	Location coordinates
Soil 1	MU 090213	Mullewa (0 cm)	a	13.4	4.8	34.5	47.2	0.75	0.58	0.75	WGS84 S28.59050785 E115.4457249
Soil 2	TL5 4	Toolibin Lake (0 cm)	a	7.8	<0.01	14.77	77.43	1.19	0.23	46.98	UTM Zone 50 N6353334 E055460
Soil 3	TL5 4 D60	Toolibin Lake (60 cm)	a	57.25	4.0	15.83	57.25	0.14	<0.10	7.04	UTM Zone 50 N6353334 E055460
Soil 4	MU 100105	Mullewa (0 cm)	b	10.1	2.2	0	0	0.35	0.26	7.60	WGS84, S28 30 19.2 E115 12 33.6
Soil 5	MU 100105w	Mullewa (0 cm)	b	4.8	0.01	22.7	72.5	0.44	0.52	8.8	WGS84, S28 30 19.2 E115 12 33.6

All determinations were conducted at CSBP Bibra Lake Western Australia (a) and ChemCentre Western Australia (b). A detailed description of each procedure is given in Indorante et al. (1990) for clay, silt and sand and in Rayment and Lyons (2011) for OC (page 68), for CaCO₃ (page 420) and for Fe-DPTA (page 240).

under the user setup (slave) can be corrected to the SBM setup by applying the following:

$$CF_\lambda = 1 - ((S\rho_\lambda - SBM\rho_\lambda)/S\rho_\lambda)$$

$$Rc_\lambda = Ro_\lambda \times CF_\lambda$$

where

$S\rho$ is the reflectance of the Slave ISS reference (the WB and LB measured at the user's setup)

$SBM\rho$ is the reflectance of the soil benchmark (SBM) ISS reference (the WB and LB sand samples measured at CSIRO-0 setup)

Ro is the original soil sample reflectance (the SOIL spectrum measured at the user's setup)

Rc is the corrected soil sample reflectance (the SOIL spectrum measured at the user's setup normalized to the CSIRO-0 setup)

CF a correction factor.

4. Results

4.1. General

Fig. 3 shows the ISS samples, LB and WB (b), and the five soil samples (a) that were selected for this study. Fig. 4 provides the ISS reflectance spectra measured using the CSIRO-0 setup. As seen in Fig. 4, the WB sample consisted of high reflectance values with small spectral features, whereas LB showed moderate reflectance baseline values, with absorption features at 1.4 μm, 1.9 μm and 2.3 μm which could be assigned to hygroscopic water (the first two) and to carbonate (the last).
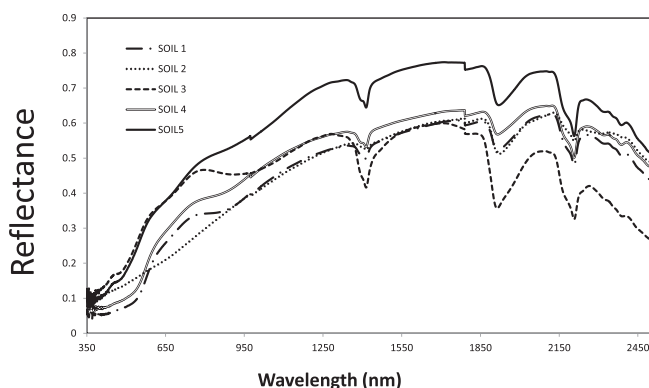
X-ray diffraction found that both samples are dominated by quartz, with LB having about 90% quartz and 10% aragonite, and WB having 99% quartz. Differential thermal analysis (DTA), thermogravimetric analysis (TGA) and gravimetric measurements demonstrated that no hygroscopic water exists in the LB sample (0.01% weight lost after 24 h in 150 °C) suggesting that the strong water spectral features at 1.4 and 1.9 μm can probably be assigned to zeolitic water trapped in the aragonite structures. TGA showed 20% loss of weight above 450 °C in the LB sample and the reflectance spectrum of this heated sample no longer showed the two water peaks at 1.4 and 1.9 mm. This demonstrates that the "zeolitic" water is trapped at higher energy than the hygroscopic water bonded to the mineral's surface. Thus, although the LB possesses a spectral signature that "looks like" soil hygroscopic water (which can vary in time and space quite significantly in high surface area minerals such as smectite; Ben-Dor et al., 1999), the real water signals may be stable in all possible room temperatures and humidifies. These characteristics make the LB an excellent sample for ISS as it holds stable features similar to soil and maintains >50% baseline reflectance. The second sample selected for the soil ISS, WB, is also a good reference, as it was found to be featureless (quartz purity, 99%) and very bright (with 90% baseline reflectance at 1.7 μm), with no hygroscopic water at all. Together with LB, WB covers the potentially high dynamic ranges for soils and thus is ideal for systematic corrections. In addition, each ISS is an independent sample for calculation of the correction factor and thus better represents the systematic variation that the ISS method stands for. We then use the average of the correction factors extracted from both ISS samples.

Table 3 provides the exact locations and some attributes of the soil samples selected to check the ISS concept and Table 4 provides the minerology of the soils as obtained from the XRD. Fig. 5 shows the spectra of these five soil samples as measured under the CSIRO-0 setup. They all exhibited typical soil reflectance features (Ben Dor, 2010) with iron oxide absorption features in the visible (VIS) region (samples 1, 3, 4, 5), an organic matter feature (sample 2) and hygroscopic water at 1.4 and 1.9 μm (all), clay at around 2.2 μm, and possible feldspar features at around 2.3–2.4 μm (See Table 4).

Fig. 5. The spectra of the five soil samples as measured by the CSIRO-0 setup.

Table 4
Mineralogy of the five soils used to examine the ISS concept, using WB and LB as ISS samples.

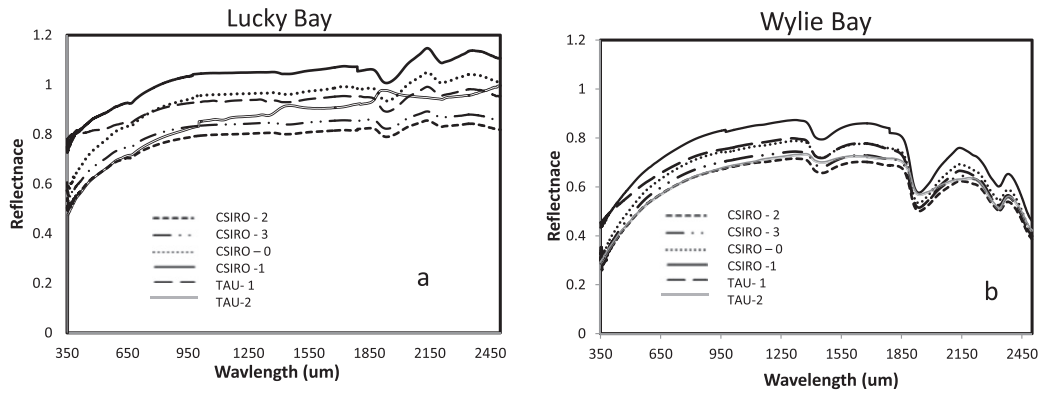| Soil number	Mineralogy (XRD)
1	Quartz (dominant), kaolinite (minor), hematite (trace), feldspar (trace)
2	Quartz (dominant), feldspar (trace), kaolinite (trace)
3	Quartz (dominant), kaolinite (minor), feldspar (trace), goethite (trace)
4	Quartz (dominant), kaolinite (minor), feldspar (trace), hematite (trace), halite (trace)
5	Quartz (dominant), kaolinite (minor), feldspar (trace), hematite (trace)

Fig. 6. The spectra of the internal soil standard (ISS) samples (LB − a, WB − b) as measured by all protocols and setups.

Fig. 6 shows the WB (a) and LB (b) spectra as measured in all of the setups used in this study for each soil. The spectral variation around the CSIRO-0 (SBM) setup is significant and mainly based on the systematic effects that occurred as part of the modifications applied. The spectral variations are mostly related to the baseline offset position whereas in TAU-2, new spectral features are observed near 1.4 and 1.9 μm. As TAU-2 setup was based on BaSO₄ as a white reference. As BaSO₄ is a hygroscopic material, the new signals at TAU-2 are related to the water molecule spectral features of the white reference. In general spectral variations from CSIRO-0 occurred either in major (TAU-2) or minor (CSIRO-1) modifications, confirming that even small changes in the reflectance measurement protocol can cause significant spectral changes in the final spectral product. This strengthens the need for a correction to be further applied to the data, and will be discussed accordingly.

To visually examine the ISS method's performance, we provide for every setup the spectra of each soil before and after the ISS correction was applied (Figs. 7–11) along with the corresponding soil spectrum of the CSIRO-0 setup (the soil benchmark configuration; SBM). To quantitatively examine the ISS method's performance, we calculated the average sum of deviation square (ASDS) index suggested by Ben-Dor et al. (2004) as follows:

$$ASDS = \Sigma \left(Sis\rho_\lambda - 1 \right)^2 / n \qquad (4)$$

$$Sis\rho_\lambda = RC\rho_\lambda / RM\rho_\lambda \qquad (5)$$

where n is the number of spectral channels of the spectrometer used to measure the soil sample, $RC\rho_\lambda$ is the reflectance value (at a given
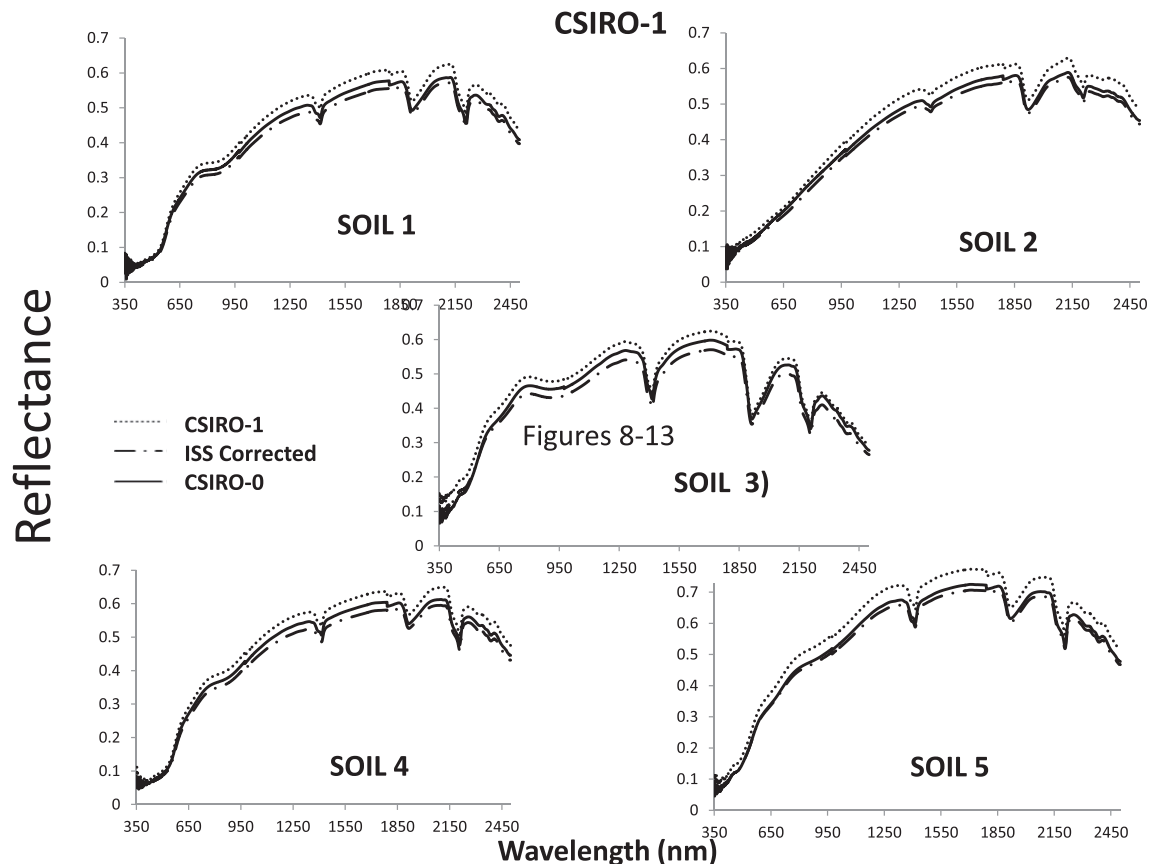

Fig. 7. The spectra of the five soil samples as measured by CSIRO-1, CSIRO-1 corrected to CSIRO-0 using the internal soil standard (ISS-Corrected) approach, and CSIRO-0.
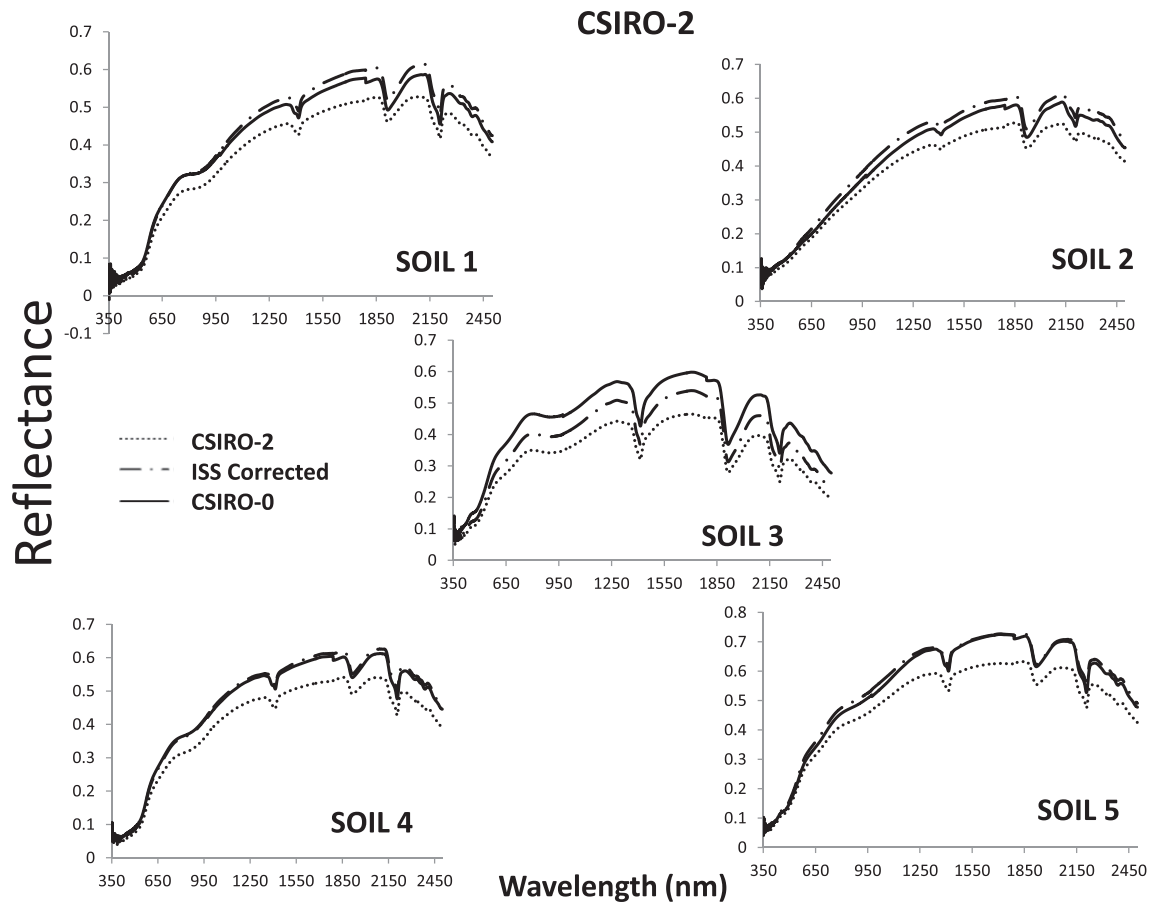
Fig. 8. The spectra of the five soil samples as measured by CSIRO-2, CSIRO-2 corrected to CSIRO-0 using the internal soil standard (ISS-Corrected) approach, and CSIRO-0.

wavelength) of the examined sample (original and ISS-corrected spectra) relative to the reflectance value (at a given wavelength) of the same soil with the benchmark setup, $RM\rho_\lambda$ (the CSIRO-0 spectrum). Lower ASDS values indicate better ISS correction performance. To judge the correction power of the ISS method, we calculated the normalized different ASDS values (ND-ASDS) according to:

$$ND\text{-}ASDS = (ASDS(b) - ASDS(a))/ASDS(b) \qquad (6)$$

where ASDS (b) is the ASDS calculated before ISS correction and ASDS (a) is the ASDS calculated after ISS correction. More positive ND-ASDS values indicated better ISS correction performance. The histograms of these calculations are given in Fig. 12 (for the ASDS) and in Fig. 13 (for the Nd-ASDS).

4.2. Interpretation of the ISS results

4.2.1. Case study 1: CSIRO-1 protocol (changes: CP with small modification of different WR (PTEE "cape"))

In Fig. 7 all of the soil spectra for this case study are shown before and after correction to the CSIRO-0 setup. Although this case study represents "minor" changes from the SBM protocol (see Table 2), spectral variations from the CSIRO-0 setup were still observed. The PTFE "cape" configuration (CSIRO-1) showed higher reflectance values relative to the brand-new PTFE disc (CSIRO-0). This demonstrates that a different PTFE, even if it is clean, may provide spectral variations, even when the other measurement factors are held constant. As further seen in Fig. 7, ISS-corrected spectra (using the ISS of the CSIRO-0 setup) shifts the CSIRO-1 reflectance data toward the CSIRO-0 SBM measurements. The ASDS values (Fig. 12) show that significant change was obtained at each of the soil after the ISS correction. The normalized difference

ASDS values (ND-ASDS, Fig. 13) varied from 27% in SOIL-1 to 90% in SOIL-5 as shown in Fig. 7 demonstrating the power of the ISS correction.

4.2.2. Case study 2: CSIRO-2 protocol (changes: DB with moderate modification to fore-optic, WR, measurement geometry, FOV)

In Fig. 8 all soil spectra of this case study are shown before and after correction to the CSIRO-0 setup. As this case study represents "moderate" changes from the SBM protocol (See Table 2), the spectral variations from the CSIRO-0 setup are moderate as well. The samples measured with the DB configuration (CSIRO-2) were all lower in their reflectance relative to the SBM reflectance (CSIRO-0). This is mainly because the geometry of the CSIRO-2 setup and the different powered light sources than the CP in CSIRO-0 and hence, produces lower reflectance in total. These systematic variations are then corrected by the ISS method to shift the CSIRO-2 results to the CSIRO-0 setup, as seen in all of the five soils that underwent the ISS correction. The ASDS values (Fig. 12) show that significant change occurred to each soil by the application of the ISS correction. The normalized difference ASDS values (ND-ASDS, Fig. 13) varied from 44% (in SOIL-1) to 88% (in SOIL-3), suggesting the ISS correction was improving the results. This observation demonstrates that moderate systematic variation can be corrected by the ISS method.

4.2.3. Case study 3: CSIRO-3 protocol (changes: DB with moderate modifications relative to CSIRO-0 and minor modifications relative to CSIRO-2—fore optic distance to the sample changed from 10 cm (CSIRO-2) to 13 cm (CSIRO-3) and the sample holder was changed from a paper dish to a petri dish. All other parameters were as with the CSIRO-2 setup)

In Fig. 9 all soil spectra of this case study are shown before and after correction to the CSIRO-0 setup. As this case study represents
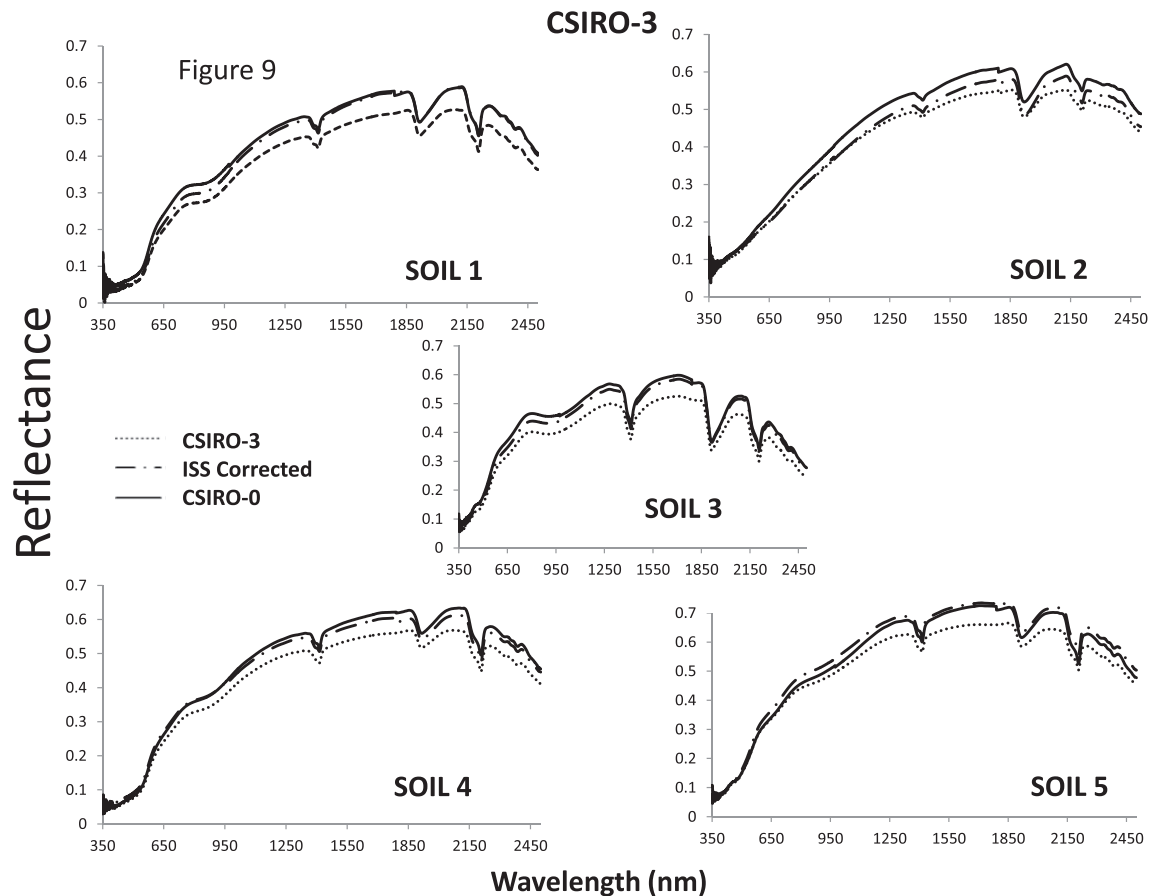
Fig. 9. The spectra of the five soil samples as measured by CSIRO-3, CSIRO-3 corrected to CSIRO-0 using the internal soil standard (ISS-Corrected) approach, and CSIRO-0.

"moderate" changes from the SBM protocol (See Table 2), the spectral variations from the CSIRO-0 setup are only slight as well. The samples measured in the DB (CSIRO-3) were all lower in their reflectance relative to the SBM reflectance (CSIRO-0) and similar to CSIRO-2 setup. This is again due to the difference in the measurement geometry relative to the CSIRO-0. These systematic variations are corrected by the ISS method to the CSIRO-0 setup, as seen in all of the five soils that underwent the ISS correction. The ISS correction aligns the CSIRO-3 reflectance data toward the CSIRO-0 SBM measurements. The ASDS values (Fig. 12) show that significant change was obtained at each soil by the ISS correction. The normalized difference ASDS values (ND-ASDS, Fig. 13) varied from 31% in SOIL-5 to 85% in SOIL-3 demonstrating again the power of the ISS correction in this moderate systematic variation set.

4.2.4. Case study 4: TAU-1 protocol 1* (changes: CP with major modifications; ASD, non stable CP assembly, WR, operator, environment and geographic locations)

In Fig. 10 all soil spectra of this case study are shown before and after correction to the CSIRO-0 setup. Although this case study represents "major" changes from the SBM protocol (see Table 2), the spectral variations from the CSIRO-0 setup are minor (SOIL-5) to moderate (SOIL-3). As seen, the samples measured in the TAU-1 setup were all systematically lower in their reflectance values relative to the CSIRO-0 SBM reflectance. This is due to fact that the illumination conditions for the TAU-1 method were dissimilar to those in CSIRO-0 (based on different bulbs, spectrometers and geometry). The total changes generate a systematic variation accordingly. The ISS corrected spectra shows favorable results in SOIL-2, SOIL-4 and SOIL-5 but small (although positive) changes to SOIL-1 and SOIL-3. The ASDS values (Fig. 12) show that

significant changes occurred to each soil by the ISS correction. The normalized difference ASDS values (ND-ASDS, Fig. 13) varied from 19% in SOIL-3 to 94% in SOIL-5 demonstrating the power of the ISS correction.

4.2.5. Case study 5: TAU-2 protocol 1* (change: CP with major modifications; ASD, non-stable CP assembly, $BaSO_4$ as WR, operator, environment, geographic locations)

In Fig. 11, all soil spectra of this case study are shown before and after correction to the CSIRO-0 setup. This case study represents "major" changes from the SBM protocol (See Table 2), where the most significant was the use of $BaSO_4$ as a white reference. The spectral variations from the CSIRO-0 setup are major, not only in the baseline shift, but also in the absorption peaks around the H_2O absorption peak at 1400 and 1800 nm and the baseline between these two wavelength regions. It is interesting to note that although these major changes were performed to the sampling method, the ISS methodology was able to correct the TAU-2 spectra and align them to the results of the CSIRO-0 setup. The ASDS values (Fig. 12) show that significant changes occurred to each soil by the application of the ISS correction. The normalized difference ASDS values (ND-ASDS, Fig. 13) varied from 36% in SOIL-1 to 62% in SOIL-4 demonstrating the power of the ISS correction in this case as well in the others.

5. General discussion

5.1. ASDS discussion

In the literature, performance of the soil proxy analysis is favored even without any standardization procedures. This is mainly due to
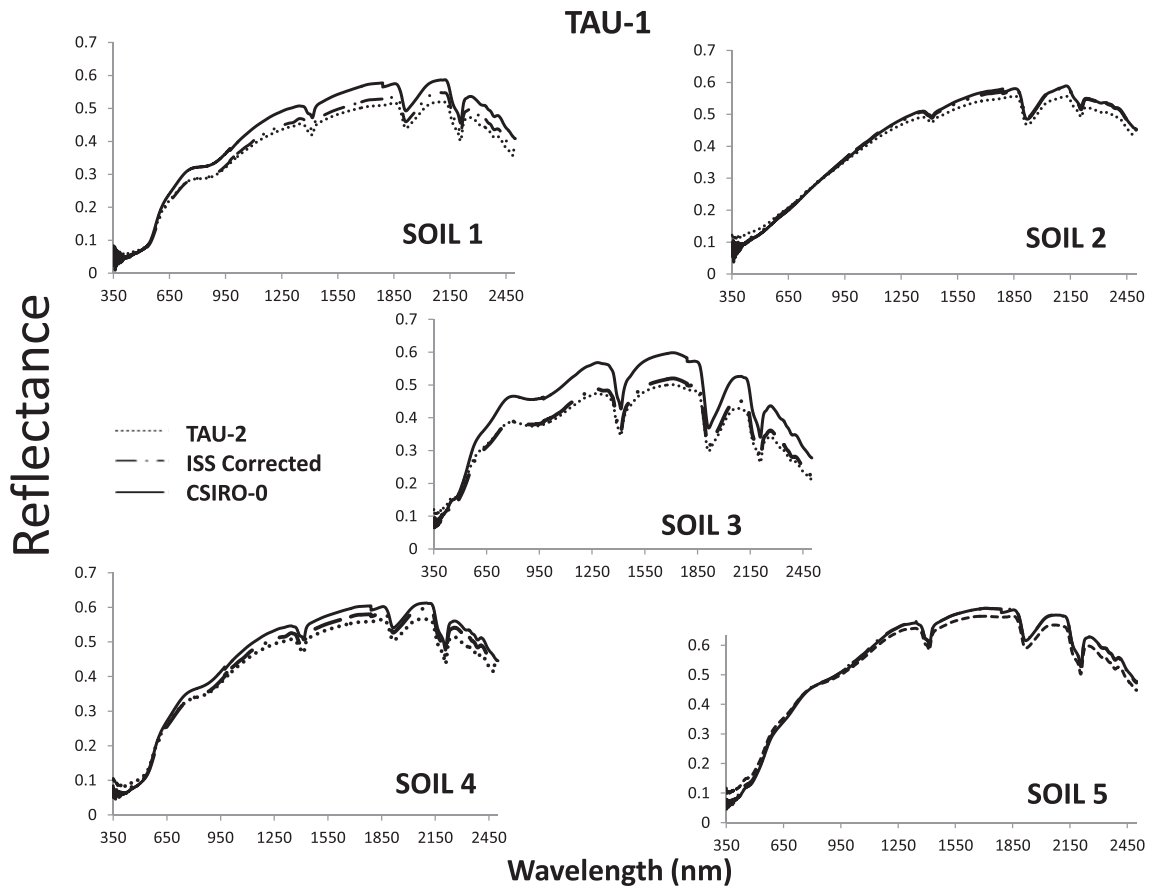
Fig. 10. The spectra of the five soil samples as measured by TAU-1, TAU-1 corrected to CSIRO-0 using the internal soil standard (ISS-Corrected) approach and CSIRO-0.

the fact that the measurement protocol for each model is usually kept constant, with the result that all of the effects related to signal are modeled along with the systematic effects. Nonetheless, if there was a need to use a model that was constructed using method A to soil measured in method B, the results may be significantly compromised by the effects of variations from the differing measurement techniques.

Accordingly, the ISS approach aims at projecting all spectral measurements (A and B in our example) as close as possible to an agreed (SBM) setup measurement, enabling the increase of the soil population (and hence accuracy) for the proxy model. Götze and Glässer (2012) have suggested using the same white reference across laboratories in order to align the variations obtain between two spectrometers. Apparently this idea is impractical as it is impossible to share the same one white reference for all users. Moreover, this study shows that not only spectrometer variations are in effect but also white reference variations are significant. It is also possible that the same white reference is deteriorating with time.

The results of this study also showed that even within a given protocol, slight (systematic) changes can occur (CSIRO-0 vs. CSIRO-1), whereas in some cases these changes are of the same magnitude with extreme changes in the measurement protocols (CSIRO-1 vs. TAU-1). The ISS solution, which was adopted from the wet chemistry discipline, showed that a correction of the results from a measurement setup to the SBM (CSIRO-0 setup) is possible. It is true that the ISS correction does not exactly shift the spectrum of a given soil to its corresponding CSIRO-0 setup measurement, but in all cases it was better aligned that without a correction, and now is closer to the CSIRO-0 results. Moreover, the ISS method also showed the possibility of correcting for spectral artifacts (such as adsorbed water on the BaSO4 white reference) enabling the biased spectrum to much better fit the original spectrum

measured using the CSIRO-0 setup. The ISS also showed the possibility to align between two different laboratories located in the northern and southern hemispheres, measured by different users, using dissimilar protocols, with different instruments and different white references. This adds to the ideas of Pimstein et al. (2011) and confirms the ISS approach in soils. The success of the ISS approach presented in this paper is a result of allocating ideal "internal soil standards" which were stable in time and space, hold "soil structural shape" and were easy to obtain. Besides using these ISS samples to align the user soil spectral measurement to a benchmark configuration it can be used to track the spectral measurement stability of the spectrometer. In this regard, it is recommended that all users measure the ISS samples prior to their sample measurement (at the exact same geometry and laboratory conditions) to track after possible deterioration of the measurement scheme.

The WB and LB samples found in Western Australia seem to be ideal materials for the Internal Soil Standard (ISS) approach, which is to correct soil spectral measurements to a SBM setup. These samples are quite homogeneous and almost monomineralic (quartz), consisting of a particle size and shape found in naturally occurring soils. They are bright (LB) and semi-bright (WB) samples (to cover large dynamic range) with stable spectral features. Accordingly, the vast worldwide effort to establish more soil spectral libraries (and extend the present ones) might be significantly benefited from the ISS approach. If the ISS method and the suggested samples were adopted by the soil spectral community it would improve the cross calibration and sharing of soil spectral databases, employ a reasonable comparison between global soils and more importantly, open the possibilities of obtaining robust proxy models to estimate soil attributes. It should also be pointed out that although this paper deals with laboratory and controlled conditions, there is an important requirement to upscale the ISS idea into the field environment.
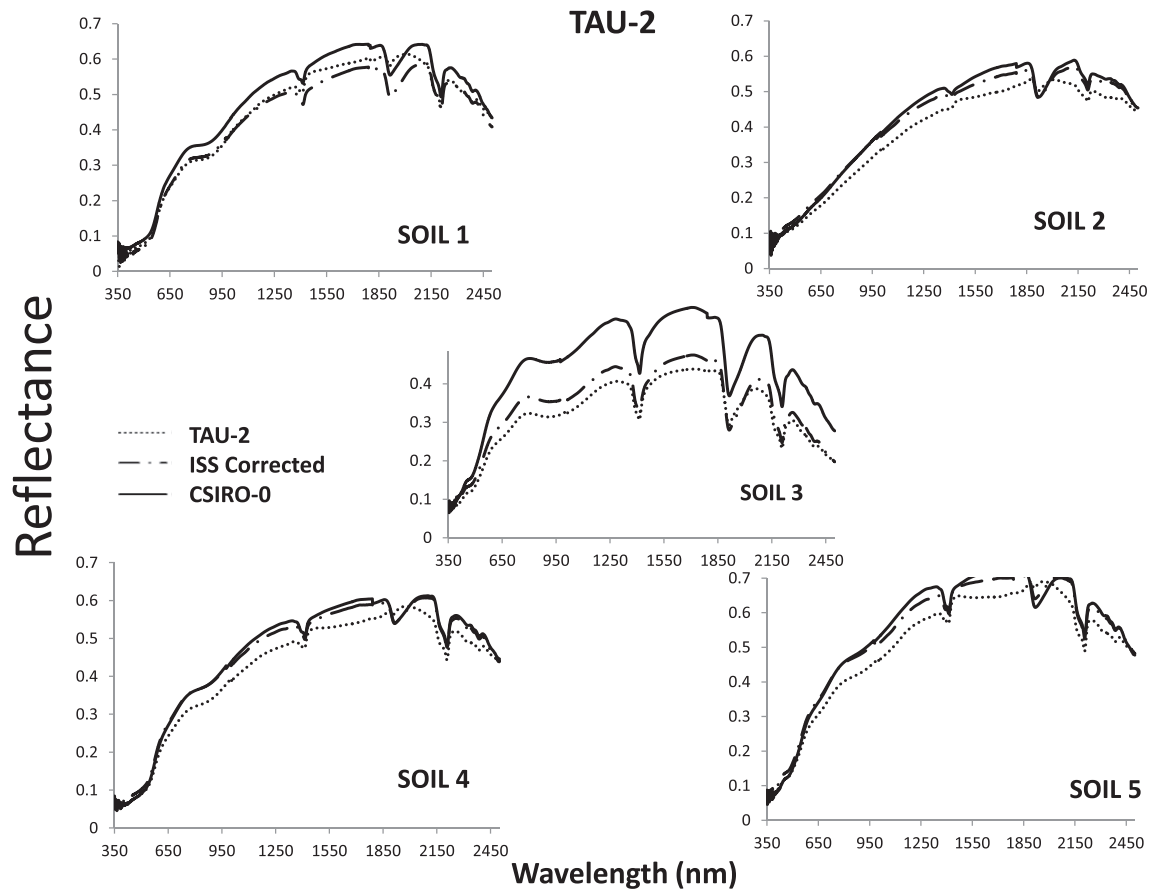
Fig. 11. The spectra of the five soil samples as measured by TAU-2, TAU-2 corrected to CSIRO-0 using the internal soil standard (ISS-Corrected) approach, and CSIRO-0.
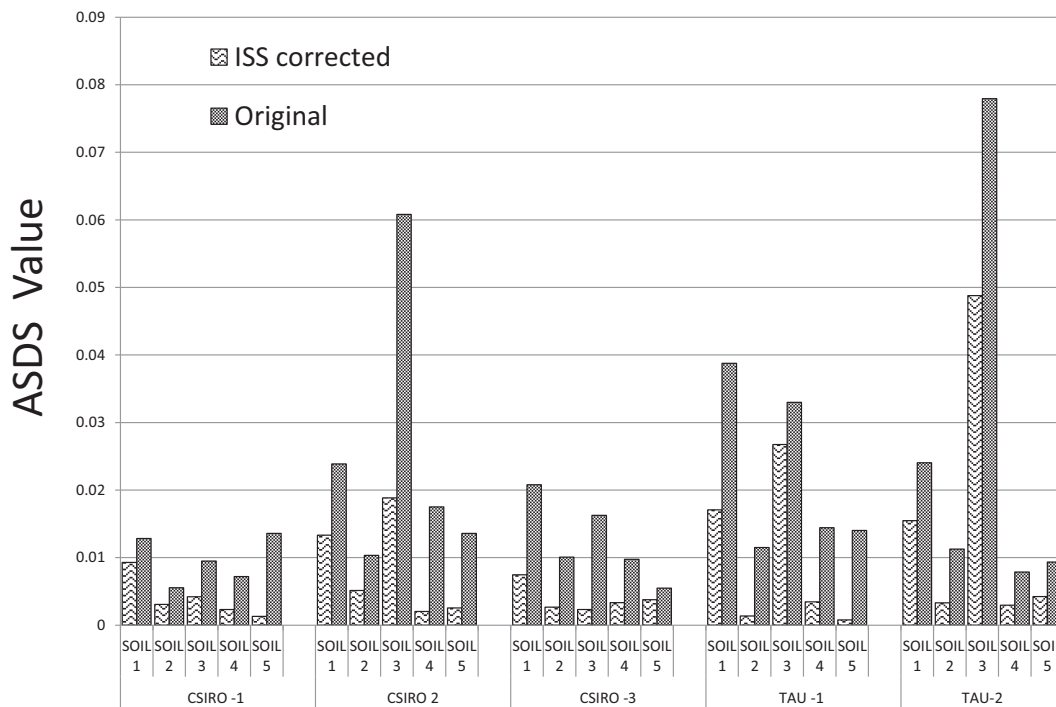

Fig. 12. Histogram showing the ASDS values (see Eqs. (4)–(6)) of each soil with each protocol relative to the SBM setup — CSIRO-0 before and after correcting it to the CSIRO-0 setup using the internal soil standard (ISS) approach, and with CSIRO-0.
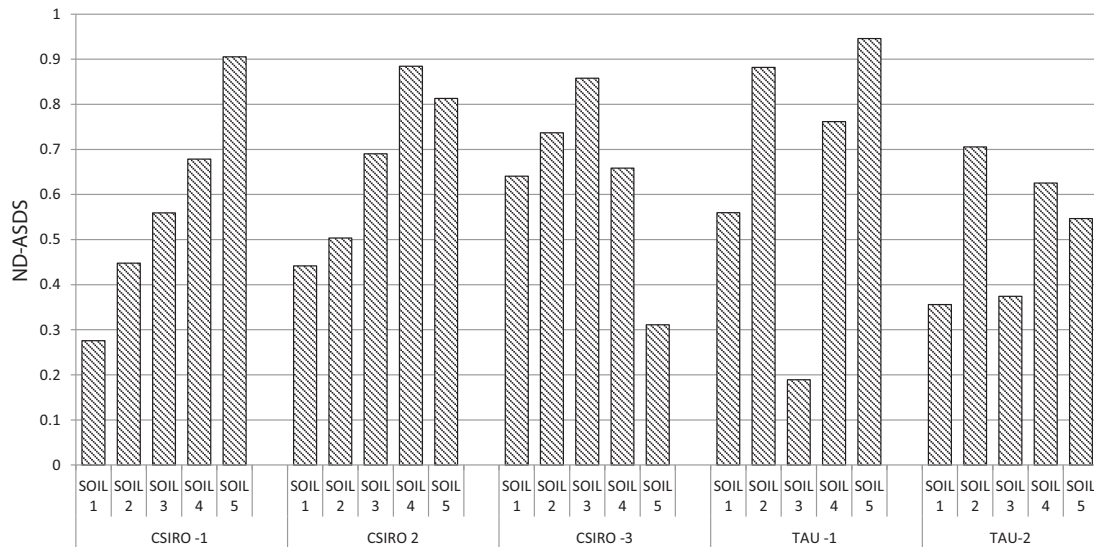
Fig. 13. Histogram showing the normalized deviation (ND) ASDS (see Eqs. (4)–(6)) of each soil with each protocol.

However, this would require more research based on the fact that more nonsystematic effects will need to be addressed and studied.

The ASDS and normalized ASDS (ND-ASDS) values are good indicators to demonstrate the performance of the ISS approach. As seen in Figs. 12 and 13, all ASDS and ND-ASDS values were positive, ranging from 20% to 89% correction capacity. In all the samples and all setups, the ISS method brought the final results closer to the SBM measurements. The ability to correct for strong systematic effects, such as the water absorption features from using $BaSO_4$ and not PTFE was shown by using the ISS approach. This demonstrated that the ISS approach is a powerful method for overcoming systematic drifts which may occur in any protocol. This suggests that the user's protocol can be retained, as long as the ISS samples are used and the protocol is kept constant. Nonetheless, although at CSIRO two soil spectral measurement protocols were developed and comprehensively examined (can be achieved as indicate later), we suggest users to adopt the method, as it is simple and cheap to construct and found to be stable and steady. The question of which is the perfect soil benchmark setup to continue the ISS approach is an important issue but not crucial. The suggested CSIRO-0 setup used here, can be easily replaced by another (agreed) setup (e.g. integrating sphere) and transferred to all users that adopted the ISS method with CSIRO-0 samples. If the same ISS sample was to be measured by a new suggested setup, a simple transformation from the CSIRO-0 setup to the new one can be done using the ISS method. The correcting factors are then applied to all of the CSIRO-0 aligned setup and a new correction database could be generated. For the time being and for all practical purposes, we strongly recommend to use LB and WB samples and the CSIRO-0 setup as the SBM entity. After collecting more data a new SBM setup may be considered.

The ISS LB and WB samples used in this study can be sent to any user via request to the authors of this paper along with their CSIRO-0 (digital) spectra. This will enable all users from hereon in to align their soil spectral information with a "common denominator" and will hopefully open a new era in the worldwide effort to combine and share all SSLs.

However, it should be pointed out that in reality, every SSL has to be accompanied by chemical information on the soil attributes. Whereas this paper deals with the spectral variation and its correction according to a simple standardization process, the same effort has to be incorporated into the chemistry section, where variation may also occur and affect the final proxy results when using SSLs from multiple sources.

6. Summary and conclusion

The ISS method to align soil spectral readings to a benchmark setup by using internal sand samples from Western Australia has proven to work successfully. It demonstrated an easy and practical way to align minor and extreme systematic changes encountered in the different protocols and setups used (using the same samples). The results of this paper confirms the ideas of Pimstein et al. (2011) and further up-scale their method by finding, analyzing, examining and preparing ideal internal soil standards for the entire soil community. The ISS method was found to mostly solve the systematic issues if a constant setup is kept for both the soil samples and for the internal soil standards. If the user protocol is extremely different from the CSIRO-0 protocol (the selected benchmark setup in this study) then the user is urged to measure the ISS samples more frequently (e.g. before and after every soil sample measurement). This is also true if nonsystemic effects are suspected to be dominant in the measurement setup (e.g. the measurement assembly is unstable). Although we strongly recommend the use of the CSIRO CP and DB protocols (see. http://dx.doi.org/10.4225/08/54992DB18BB6E), this is not mandatory as long as the user protocol is stable, reliable and reputable, and followed by the exact ISS samples (LB and WB) measured at CSIRO-0 (or later, under another agreed-upon benchmark setup). The LB and WB samples can be also used to track the performance of the used protocol and the temporal performance of the instrumentation. Based on the results of this paper, we hope that users will now adopt the ISS method in every soil spectral measurement they conduct and the forthcoming spectral data will hold a well-agreed-upon standardization quality that will enable sharing and comparing soil spectral data in a newly beneficial way.

Acknowledgments

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