

Introduction

Contemporary environmental studies, including soil testing, is becoming more and more quantitative and thus requires implementation of numerous expensive and time-consuming tests. Financial and time limitations induce the development of new methods for indirect determination of various soil properties. Visible and near infrared (VNIR) diffuse reflectance spectroscopy (DRS) has proven to be a rapid and effective method of providing reliable data for soil monitoring, digital soil mapping, environmental modeling, and precision agriculture. Comprehensive lists of published investigations on DRS of soil properties have been presented recently. The presented study was performed to investigate the possibility of application of DRS measurements in monitoring of arable soils chemistry.

Materials and Methods

During the program “Monitoring of Chemistry of Arable Soils”, in 2005, 212 soil samples from the surface layer (0 - 20 cm) were acquired from throughout the area of arable lands in Poland, covering approximately 140000 km². In these samples the following characteristics were determined: textural composition (8 fractions); contents of organic carbon (Corg) and organic matter (OM), total nitrogen (N-Kjeldahl), carbonates; plants available forms of phosphorus (P₂O₅), potassium (K₂O), magnesium (MgO) and sulfur (S-SO₄); polycyclic aromatic hydrocarbons (PAHs); “total” forms of S, P, Na, K, Ca, Mg, Fe, Al., Mn, Cu, Ni, Cr, Zn, Cd, Co, Pb, Ba, Be, La, Li, Sr. exchangeable forms of Ca, Mg, K, Na, hydrolytic and exchangeable acidity (Hh, Hw), cation exchange capacity (CEC), sum of bases (TEB), degree of base saturation (BS) and C:N, ratio were calculated. Electrical conductivity (EC), soil salinity, radioactivity and pH (in water and KCL) were also measured. All analysis were conducted in laboratories of the Institute of Soil Science and Plant Cultivation in Puławy.

Reflectance r of soil samples was measured in five replications at the wavelength range from 350 nm to 2500 nm, at 1-nm intervals, using a FieldSpec®Pro spectroradiometer (Analytical Spectral Devices, Inc., Boulder, CO, USA) with the attached Source Probe Mug-Lite®. DSR data were generalized into 10-nm intervals and transformed into root of r , $1/r$, absorbance, first and second derivative of r , Kubelka Munk units and its derivative and continuum removal values. Correlation between reflectance and soil properties were calculated for the total dataset and for the clusters obtained by unsupervised Ward hierarchical algorithm based on Euclidian distance (StatistiXL - Nedlands, Australia).

Results

Spectral curves of 212 soil samples and clustering results are presented in figure 1. Coefficient of determination between DSR and soil properties obtained on total dataset were lower than values for clustered data (Tab. 1). Only total forms of Ca and Sr can be estimated from spectral data without clustering. After clustering of entire dataset the strongest relationships were observed between reflectance data and soil total concentration of Zn, Ni, Cu, Ba, Be, Li, Co, Cr, Mn, Fe, Al, K, Mg, S, exchangeable cations (TEB and CEC), radioactivity and contents of Corg, N-kjel., CaCO₃, clay and sand fraction,

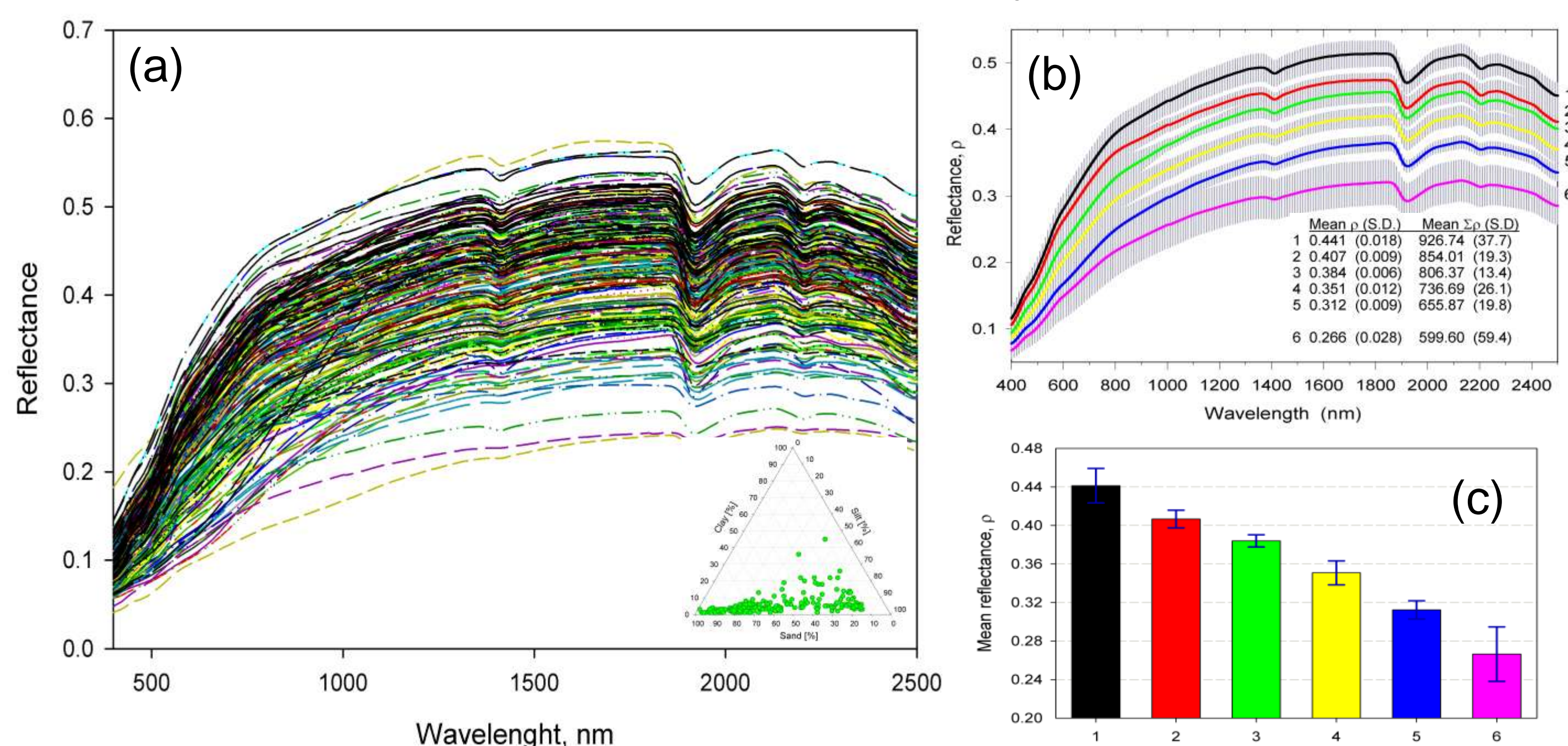


Fig. 1. Spectra of 212 soil samples of arable fields in Poland (a), mean spectra and its standard deviation for six clusters obtained by Ward algorithm (b) and the differences of mean clusters spectra (c).

Table 1. Mean and maximum coefficient of determination between DSR transformation and soil properties on the total dataset and clusters

Forms*	Units	Mean R ² on total data	Maximum R ² on total data	Mean R ² in clusters						Average clusters means R ²	Average clusters max R ²	Prediction possibility using DSR **
				1	2	3	4	5	6			
OM	ORG. %	0.048	0.193	0.155	0.066	0.250	0.113	0.083	0.080	0.155	0.464	-
C:N	-	0.017	0.069	0.012	0.054	0.054	0.036	0.048	0.166	0.012	0.245	-
P	TC %	0.030	0.147	0.091	0.076	0.106	0.069	0.078	0.203	0.091	0.383	-
P-P ₂ O ₅	P.A. mg P ₂ O ₅ 100g ⁻¹	0.015	0.054	0.021	0.021	0.025	0.033	0.050	0.020	0.021	0.283	-
S-SO ₄	P.A. mg SO ₄ 100g ⁻¹	0.008	0.052	0.064	0.033	0.048	0.046	0.007	0.112	0.064	0.229	-
K-K ₂ O	P.A. mg K ₂ O 100g ⁻¹	0.030	0.184	0.039	0.023	0.086	0.124	0.108	0.098	0.039	0.363	-
Salinity	mg KCl 100g ⁻¹	0.034	0.155	0.043	0.086	0.052	0.070	0.119	0.101	0.043	0.383	-
EC	mS m ⁻¹	0.034	0.156	0.043	0.083	0.053	0.071	0.119	0.102	0.043	0.384	-
pH H ₂ O	-	0.029	0.156	0.097	0.070	0.053	0.051	0.060	0.187	0.097	0.401	-
pH KCL	-	0.030	0.144	0.087	0.064	0.044	0.098	0.076	0.177	0.087	0.393	-
Hh	EXCH. mmol(+) kg ⁻¹	0.033	0.171	0.095	0.040	0.036	0.035	0.118	0.177	0.095	0.387	-
K	EXCH. mmol(+) kg ⁻¹	0.047	0.266	0.090	0.050	0.114	0.113	0.113	0.108	0.090	0.415	-
Cd	T.C. mg kg ⁻¹	0.034	0.072	0.031	0.029	0.065	0.070	0.038	0.106	0.031	0.418	-
Pb	T.C. mg kg ⁻¹	0.152	0.178	0.015	0.039	0.044	0.163	0.059	0.332	0.015	0.352	-
PAHs-13	T.C. µg 100g ⁻¹	0.075	0.122	0.064	0.025	0.048	0.059	0.031	0.135	0.064	0.308	-
PAHs-9	T.C. µg 100g ⁻¹	0.080	0.128	0.065	0.026	0.048	0.057	0.030	0.133	0.065	0.308	-
Na	EXCH. mmol(+) kg ⁻¹	0.086	0.265	0.134	0.148	0.244	0.057	0.183	0.088	0.134	0.487	- / (SCDS)
BS	%	0.073	0.303	0.098	0.112	0.129	0.138	0.161	0.110	0.098	0.488	- / (SCDS)
La	T.C. mg kg ⁻¹	0.179	0.359	0.054	0.095	0.182	0.146	0.084	0.117	0.054	0.479	- / (SCDS)
Na	T.C. mg kg ⁻¹	0.039	0.531	0.197	0.163	0.166	0.045	0.048	0.079	0.197	0.480	- / (SCDS)
Sand	%	0.287	0.491	0.098	0.088	0.225	0.156	0.130	0.166	0.098	0.544	+ SCDS
Silt	%	0.305	0.411	0.064	0.037	0.232	0.142	0.091	0.169	0.064	0.478	+ SCDS
Clay	%	0.173	0.620	0.202	0.342	0.213	0.260	0.249	0.191	0.202	0.748	+ SCDS
C	ORG. %	0.055	0.228	0.155	0.032	0.263	0.113	0.106	0.089	0.155	0.493	+ SCDS
N - Kjeld.	%	0.066	0.291	0.172	0.116	0.204	0.157	0.124	0.117	0.172	0.544	+ SCDS
CaCO ₃	%	0.139	0.966	0.734	0.780	0.645	1.000	0.360	0.518	0.734	0.991	+ SCDS
Hw	EXCH. mmol(+) kg ⁻¹	0.031	0.256	0.122	0.242	0.125	0.044	0.141	0.189	0.122	0.647	+ SCDS
Al.	EXCH. mmol(+) kg ⁻¹	0.026	0.272	0.136	0.235	0.114	0.049	0.138	0.202	0.136	0.663	+ SCDS
Ca	EXCH. mmol(+) kg ⁻¹	0.106	0.418	0.241	0.246	0.210	0.153	0.290	0.125	0.241	0.636	+ SCDS
Mg	EXCH. mmol(+) kg ⁻¹	0.125	0.515	0.174	0.300	0.191	0.214	0.181	0.158	0.174	0.657	+ SCDS
TEB	EXCH. mmol(+) kg ⁻¹	0.112	0.450	0.239	0.251	0.225	0.164	0.286	0.134	0.239	0.655	+ SCDS
CEC	EXCH. mmol(+) kg ⁻¹	0.117	0.467	0.250	0.274	0.237	0.187	0.280	0.127	0.250	0.667	+ SCDS
Mg-MgO	P.A. mg MgO 100g ⁻¹	0.096	0.378	0.095	0.244	0.139	0.063	0.213	0.204	0.095	0.545	+ SCDS
S	T.C. %	0.048	0.228	0.199	0.063	0.156	0.092	0.122	0.148	0.199	0.521	+ SCDS
Al.	T.C. %	0.159	0.561	0.218	0.221	0.185	0.167	0.197	0.140	0.218	0.674	+ SCDS
Fe	T.C. %	0.169	0.559	0.237	0.262	0.278	0.198	0.128	0.175	0.237	0.694	+ SCDS
Zn	T.C. mg kg ⁻¹	0.033	0.073	0.097	0.128	0.170	0.087	0.037	0.108	0.097	0.510	+ SCDS
Mn	T.C. mg kg ⁻¹	0.099	0.337	0.116	0.142	0.104	0.184	0.112	0.229	0.116	0.523	+ SCDS
Cu	T.C. mg kg ⁻¹	0.021	0.090	0.035	0.199	0.185	0.097	0.081	0.177	0.035	0.561	+ SCDS
Ba	T.C. mg kg ⁻¹	0.103	0.443	0.128	0.216	0.180	0.203	0.125	0.193	0.128	0.588	+ SCDS
Be	T.C. mg kg ⁻¹	0.167	0.572	0.187	0.268	0.269	0.231	0.163	0.133	0.187	0.668	+ SCDS
V	T.C. mg kg ⁻¹	0.156	0.556	0.176	0.260	0.236	0.225	0.151	0.158	0.176	0.679	+ SCDS
Co	T.C. mg kg ⁻¹	0.135	0.469	0.182	0.148	0.236	0.132	0.168	0.296	0.182	0.707	+ SCDS
K	T.C. mg kg ⁻¹	0.137	0.643	0.214	0.241	0.235	0.226	0.211	0.150	0.214	0.707	+ SCDS
Li	T.C. mg kg ⁻¹	0.144	0.587	0.205	0.241	0.234	0.156	0.094	0.136	0.205	0.710	+ SCDS
Cr	T.C. mg kg ⁻¹	0.177	0.607	0.238	0.225	0.284	0.212	0.160	0.160	0.238	0.725	+ SCDS
Mg	T.C. mg kg ⁻¹	0.116	0.477	0.217	0.247	0.245	0.222	0.190	0.097	0.217	0.732	+ SCDS
Ni	T.C. mg kg ⁻¹	0.153	0.569	0.233	0.169	0.228	0.245	0.159	0.172	0.233	0.761	+ SCDS
Radioactivity	Bq kg ⁻¹	0.161	0.421	0.153	0.139	0.225	0.119	0.059	0.106	0.153	0.537	+ SCDS
Ca	T.C. mg kg ⁻¹	0.053	0.945	0.190	0.210	0.208	0.093	0.198	0.103	0.190	0.652	+ TDS
Sr	T.C. mg kg ⁻¹	0.054	0.844	0.195	0.116	0.178	0.113	0.132	0.169	0.195	0.651	+ TDS

Transformation codes:

*Forms of expression: T.C. - total concentration, P.A. - plant available form, EXCH - exchangeable cations, ORG - organic, **SCDS - spectrally clustered dataset, TDS - total dataset

Soil reflectance data can not be used to predict soil reaction; C:N ratio; P₂O₅, K₂O and S-SO₄, Hh and BS; salinity and EC; “total” forms P, Cd, Pb, La and Na exchangeable K and PAHs. The most useful mathematical transformation of spectral data for modeling soil properties were second derivative of raw data, first derivatives of absorbance and Kubelka-Munk unit and continuum removal. However, non of these transformation can be concerned as “universal”. Therefore, the more effective method of soil properties assessment is clustering of a spectral soil library into groups according to spectral characteristics [7] and development of regression models (e.g. partial least squares methods) and various transformations of spectral data.

Conclusion

The results of analysis confirm the relationship between DSR data and various soil chemical properties, what make possible use these techniques for lower cost and saving time in soil monitoring. The unsupervised clustering of spectral dataset into spectrally similar subsets has a potential to increase the usefulness of DRS data for the estimation of soil chemical properties. Besides unsupervised clustering, for these purposes various mathematical transformation of row data should be implemented. Because, no one of available transformation is advantageous and in particular groups of soils (clusters) specific soil properties should be determined on the basis of different transformation of spectral data.